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Reversible Oxygen Gas Sensor Based On Electrochemiluminescence

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Abstract

A novel and robust oxygen gas sensor based on electrochemiluminescence of $\text{Ru}(\text{bpy})_3^{3+/+}$ ion annihilation in an ionic liquid is presented. Real-time detection of environmental oxygen concentration together with selective, sensitive and reversible performance is demonstrated.

The development of gas oxygen sensors is still a leading priority for many applications. Despite the significant advances made in the field, a reliable, long operational lifetime, fast response, low cost, and a compact size oxygen sensor represents a formidable challenge. Solid electrolyte oxygen sensors and galvanic cell oxygen sensors are currently the most widely used sensors for monitoring oxygen gas. The solid electrolyte ($\text{ZrO}_2/\text{Y}_2\text{O}_3$) sensors typically rely on oxygen ion conductance generated at expense of high power consumption (400–600 °C), and the galvanic cell oxygen sensors are based on environmentally poisoning and limited lifetime anode materials (lead)[1]. Electrochemical sensors for oxygen detection also fall short in the stability and immunity to environmental conditions (e.g. humidity) due to their dependence on liquid electrolytes or water electrolytic reactions[2]. Furthermore, optical oxygen sensors based on fluorescence [3] and chemiluminescence [4] quenching have been reported, but they have not been widely used for various reasons. Here, we present a novel oxygen gas sensor based on electrochemiluminescence (ECL) to meet the mentioned challenges. ECL is the process whereby species generated at electrodes undergo high-energy electron-transfer reactions to form excited states that emit light [5]. Compared to many ECL systems, $\text{Ru}(\text{bpy})_3^{2+}$ -based systems gain more attention due to its high efficiency to convert electric energy into photonic energy [6,7]. The ECL sensor described in this work is based on combined operations of $\text{Ru}(\text{bpy})_3^{2+}$ electrochemical reactions, luminescence homogeneous chemical reactions, and unique properties of an ionic liquid (IL) (Figure 1A). Unlike the previous oxygen sensors that rely on the oxygen electrochemical activity, the present sensor is based on $\text{Ru}(\text{bpy})_3^{2+}$ oxidation-reduction reactions to generate a luminescent product that interacts with oxygen via quenching. This approach affords not only increased sensitivity provided by the luminescence quenching but also selectivity as evident from the demonstrated low interference level of other gases (see below).

A basic version of our sensor is formed using merely a silicon photodiode (Edmund Optics) with an integrated amplifier (Sensitivity: 0.12 V/nW, noise: 7.00 $\mu\text{Vrms}/\text{Hz}^{1/2}$), a small potentiostat, and a printed carbon electrode chip (with an electrode dimension of ~3 mm) covered with a thin layer of ionic liquid. Excellent selectivity is achieved because of several factors: (1) the control of the working electrode potential through a cyclic voltammetry

sweep to produce $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$, which in turn produce the excited species ($\text{Ru}(\text{bpy})_3^{2+*}$) responsible for photon generation through an ion annihilation reaction (Figure 1B) [5,8], (2) the specific interactions between oxygen and one of the photon generating species. In addition, the sensor hardware can be further simplified and miniaturized by the use of a microcontroller-based potentiostat [9], and an integrated photodiode power source, making the device highly portable and low cost.

One essential element of this approach is the use of the thin layer ($\sim 200 \mu\text{m}$) of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF_4) which provides the medium necessary to achieve the electrochemical reactions of $\text{Ru}(\text{bpy})_3^{2+}$ (reduction), which are not possible in conventional ECL using aqueous electrolytes [5,10]. We coat the electrode with a $200\text{-}\mu\text{m}$ thick $\text{Ru}(\text{bpy})_3^{2+}$ saturated IL film (Figure 1B). The BMIM-BF_4 coating provides (1) a medium with oxygen diffusion coefficients that are higher than those in a solid electrolyte, (2) an electrolyte of high conductivity at room temperature and high stability under extreme temperatures for long periods of time (> 6 months) [11], (3) an electrolyte that allows for reversible cycling of $\text{Ru}(\text{bpy})_3^{2+}$ species without net consumption of chemicals or electrode materials (Figure 1B), and (4) a medium that promotes the necessary stability of species involved in electrochemical, chemical and oxygen quenching reactions. We implemented the ECL-ionic liquid based platform to detect oxygen concentration levels in ambient air in the presence of various interferents.

Curve b in Figure 2 is a cyclic voltammogram of $\text{Ru}(\text{bpy})_3^{2+}$ in IL, which shows the oxidation and reduction processes associated to $\text{Ru}(\text{bpy})_3^{2+}$. The peak current is proportional to the square root of the scan rate, indicating a diffusion-controlled process. Furthermore, the simultaneously recorded ECL signal is shown as curve B in Figure 2 (between $+1.9$ and -1.9 V vs Ag/AgCl). No ECL effect was observed in absence of $\text{Ru}(\text{bpy})_3^{2+}$, confirming that the ECL signal was purely due to the ruthenium complex (Figure 2, curve A). In addition, the ECL response at positive potentials (e.g., $+1.9 \text{ V}$) was higher than that at negative potentials (e.g., -1.9 V), implying that $\text{Ru}(\text{bpy})_3^+$ is more stable than $\text{Ru}(\text{bpy})_3^{3+}$ in the present system (Figure 1B) [12]. We noticed that some potential cycles were required to pre-condition the system until a stable ECL signal was reached, which may be attributed to the removal of impurities from air dissolved in the electrolyte by the potential cycling. However, once a stable signal was established, the detection could repeatedly cycled for over 100 times between $+2 \text{ V}$ and -2 V with little variations (less 7.5 %).

It is worthy mentioning that besides the interesting application of oxygen detection presented in this communication, the intrinsic transduction mechanism of the sensor represents an advance in ECL-based chemical sensors and could find many other applications [13].

We demonstrated the capability to maintain steady chemiluminescence signals in the IL without requiring the use of toxic volatile solvents [14], or co-reagents such as alkylamines typically used in aqueous based ECL sensors [15]. In addition to providing a desirable medium to promote stable photogenic species, the IL can be easily spread in thin films of few hundreds of microns, providing an ideal interface for gas phase detection. Figure 3A shows the response of the ECL sensor to different oxygen concentrations. The oxygen concentration was adjusted by mixing different ratios of oxygen and argon (or nitrogen) with a gas diluter (Custom Sensor Solutions, Oro Valley, AZ) and the gas mixtures were injected for 5 min before each measurement to ensure uniform mixing. The ECL signal decreased with increasing oxygen concentrations. Although the effect of oxygen on the ECL signal was assigned to the oxidizing power of oxygen on $\text{Ru}(\text{bpy})_3^+$ (Figure 1B) [16], further characterization studies of the oxygen reaction products would be necessary to complete the description of the detection reaction. Nevertheless, the oxygen concentration dependence of

the ECL intensity was consistent with the fluorescence quenching described by Stern–Volmer equation: $I_0/I = 1 + K_q[O_2]$, where I_0 and I are the ECL intensities in the absence and presence of oxygen, respectively, and K_q is the quenching constant rate. The linear range for oxygen detection was from 0 to 40 % (Figure 3B). The K_q for ECL responses were 0.013 and 0.055 %⁻¹ at 1.9 and -1.9 V respectively, implying the oxygen quenching at negative potentials were more efficient compared to the ones at positive potentials. These magnitude of these quenching constants are comparable to other constants reported for fluorescence quenching systems [17].

The fast diffusion of oxygen within IL as well as the relatively high quenching efficiency of the system are responsible for the fast response time of the system and high sensitivity. The response time was a few minutes and the achieved detection limit was 3% of oxygen. However, based on the noise level of the ECL output signal (7.00 $\mu V_{rms}/Hz^{1/2}$), the estimated detection limit (for 1Hz data resolution and three times the noise level) is 0.04%. The current detection limit could be further improved by using a more efficient oxygen reaction chamber geometry and more compact system design.

We have also demonstrated highly selective detection of oxygen with various common environmental interferents at realistic interferent concentration levels. As shown in Figure 4A, when 5 % CO₂, 1 ppm NO₂, 1 ppm SO₂, 1 ppm NO and 1 ppm CO were injected into the sensor chamber, no obvious quenching was observed. However, when 20% O₂ (atmospheric typical concentration) was injected, ECL signal was quenched to ~ 39 % of the initial level. In order to ensure the utility of the sensor we have interrogated it with oxygen concentration dilutions treated as unknown samples (Figure 4B). We found a correlation with an slope of 0.95 between the oxygen concentration levels from the ECL sensor and nominal oxygen concentration of the samples and an average dispersion of less than 3% with a 95% level of confidence. These results were reproducible over different days and for different sensors, which demonstrated the robustness of the ECL oxygen sensor.

Conclusions

We developed a new gas oxygen sensor based on ECL by integrating Ru(bpy)₃²⁺ embedded in a thin film of IL. Oxygen chemiluminescence quenching in an IL is demonstrated for the first time. The sensor, based on environmentally-friendly and long lasting materials, overcomes known difficulties of existing oxygen sensor technologies. Reversibility of the sensor response is possible because of the use of the photogenic Ru(bpy)₃²⁺ complex in combination with IL. High sensitivity and selectivity are achieved by an intrinsic oxygen quenching process. Using an inexpensive solid state photodiode and a potentiostat circuit, we have achieved low detection limits of oxygen with a wide dynamic range that is suitable for environmental safety applications. In addition, a compact size sensor is feasible with the configuration of the present system.

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Figure 1.

(A) Representative scheme of the oxygen sensor based on ECL phenomena. (B) Picture of the electrodes coated with a layer of 200 μm of IL saturated with $Ru(bpy)_3^{2+}$, and electrochemical, chemical and luminescence reactions responsible for the sensor transduction mechanism.

Figure 2. Cyclic voltammograms and ECL responses in IL (a, A) and in IL containing Ru(bpy)₃²⁺ (b, B).

Figure 3. (A) ECL response of the present sensor to 0, 10%, 20%, 30% and 40% O_2 . (B) Linear calibration plots of ECL response for O_2 at +1.9 V (empty symbol) and -1.9 V (full symbol) respectively.

Figure 4.

(A) ECL responses at -1.9 V for 5% CO₂, 1 ppm NO₂, 1ppm SO₂, 1ppm NO, 1ppm CO and 20% O₂. (B) Correlation plot between oxygen levels assessed with the ECL sensor and the nominal oxygen levels of the ambient samples (Slope = 0.95, relative error: 2.8 %).