O_2 Gas Sensor Using Supported Hydrophobic Room-temperature Ionic Liquid Membrane-coated electrode

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A solid-state amperometric O_2 gas sensor was successfully fabricated by using supported 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$) porous polyethylene membrane as a solid-state electrolyte. The present O_2 gas sensor, which is capable of being operated at room temperature, shows a wide detection range and a high stability.

Recently, room-temperature ionic liquids (RTILs) have been used in many areas of chemistry, and may also be useful for fabricating gas sensors,[1] as they have low melting point, wide electrochemical window, and high solubility for a wide range of materials. Especially, a high ionic conductivity of RTIL at room temperature allows the gas sensor to operate at room temperature. In addition, a negligible vapor pressure of RTILs does not cause the drying out of the electrolyte which is a serious problem for the sensors using solid polymer electrolyte films.[2] In this letter, a novel solid-state amperometric O_2 gas sensor based on the supported $BMIPF_6$ membrane will be proposed.

Figure 1 shows the schematic representation of the electrochemical measurement system used in this study, in which the supported $BMIPF_6$ membrane was prepared by soaking up the porous polyethylene membrane (7P03A, Teijin Solufill Co., Japan) in $BMIPF_6$ solution (Fluka) for at least 1 day under reduced pressure at 30 °C. The obtained supported $BMIPF_6$ membrane was then closely mounted on the surface of the epoxide resin disk, in which a three-electrode system was constructed, to fabricate the O_2 gas-sensing electrode system. The dried pure O_2 (or N_2) gas, water-saturated pure O_2 (or N_2) gas and dried O_2–N_2 gas mixtures used in the electrochemical measurements were introduced through the gas flowing-routes a, b, and c shown in Figure 1, respectively.

The redox behavior of O_2 at the $BMIPF_6$ membrane-coated electrode is shown in Figure 2. In dried O_2 atmosphere, a couple of redox peaks were observed on the CV (voltammogram (b)) with formal potential at ca. -0.66 V vs Ag, which is similar to that obtained for O_2 reduction in $BMIPF_6$ solution.[3] Thus, the observed cathodic and anodic peaks can be assigned to the one-electron reduction of O_2 to superoxide ion ($O_2^{-\bullet}$) and the reoxidation of $O_2^{-\bullet}$ to O_2, respectively. This well-defined CV also indicates that the supported $BMIPF_6$ membrane has a high ionic conductivity at room temperature. In water-saturated O_2 atmosphere (voltammogram (c)), the cathodic peak potential shifted positively and the cathodic peak current value increased about twice compared with that obtained in dried O_2 atmosphere. Thus, the new cathodic peak at about -0.7 V can be assigned to the two-electron reduction of O_2 to H_2O_2.[4] In addition, the anodic peak at ca. -0.53 V disappeared and two new anodic peaks at 0.35 V and ca. 1.0 V were observed. These two new anodic peaks can be regarded as the reoxidation of H_2O_2. After measuring voltammogram (c), the electrode system was held in dried O_2 gas atmosphere for 3 min, and then the voltammogram (d) was obtained. The voltammogram (d) slightly negatively shifted compared with voltammogram (b), probably due to the potential change of the Ag quasi-reference electrode. The repeated intro-

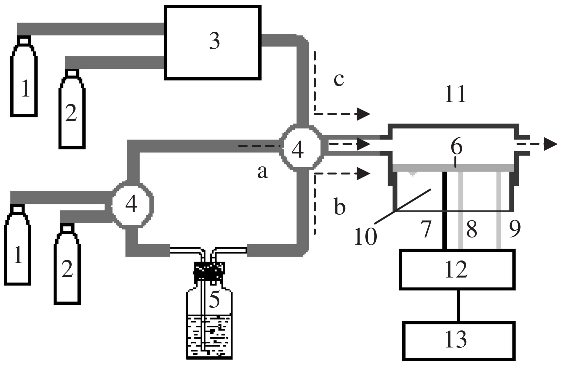

Figure 1. Schematic representation of the electrochemical measurement system used in this study. (1) N_2 gas tank, (2) O_2 gas tank, (3) gas blender, (4) valve, (5) bottle containing Milli-Q water, (6) supported $BMIPF_6$ membrane, (7) GC disk (diameter: 1 mm) working electrode, (8) Ag disk (diameter: 1 mm) reference electrode, (9) Pt ring (width: 1 mm, length: 50 mm) counter electrode, (10) epoxide resin, (11) O_2 gas-sensing electrode system, (12) potentiostat and (13) computer.

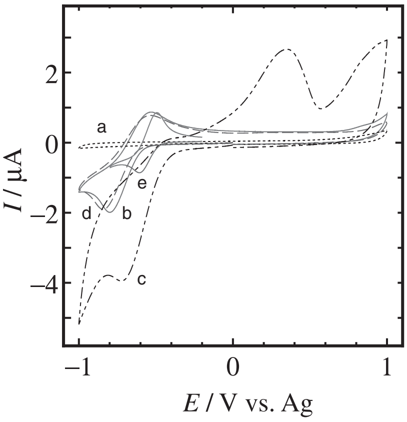

Figure 2. Cyclic voltammograms (CVs) obtained at the supported $BMIPF_6$ membrane-coated electrode at 25 ± 1 °C under (a) dried N_2 gas, (b, d) dried O_2 gas, and (c) water-saturated O_2 gas atmospheres. After measuring voltammogram (c), the electrode system was held in dried O_2 gas atmosphere for 3 min, and then voltammogram (d) was obtained. Voltammogram (e) was obtained at supported $EMIBF_4$ membrane-coated electrode under dried O_2 atmosphere. Scan rate was 100 mV s^{-1}.

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duction and removal of moisture resulted in the reproducible voltammograms of (c) and (d), respectively. Thus, we found that the water contained in the O_2-sensing electrode system changed the reduction of O_2 from one-electron reaction to two-electron reaction, but the water in the electrode system could be easily removed by holding the electrode system in dried O_2 gas atmosphere for ca. 3 min (Figure 2), and thus, the electrode system can be recovered as a result of the fact that the solid-state electrolyte membrane was composed of the hydrophobic materials, i.e., $BMIPF_6$[4] and porous polyethylene membrane. Figure 2 also shows the CV (voltammogram (e)) obtained at 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) membrane-coated electrode in dried O_2 atmosphere. As $EMIBF_4$ is a hydrophilic ionic liquid, compared with $BMIPF_6$, the saturated concentration of O_2 in the supported $EMIBF_4$ membrane is lower and consequently the smaller redox response was obtained at the $EMIBF_4$ membrane-coated electrode (voltammograms (b) and (e)).

Potential-step chronoamperometry was used to characterize the supported $BMIPF_6$ membrane-coated electrode system as an O_2 gas sensor. The potential-time waveform of potential-step chronoamperometry and chronoamperometric current responses obtained for different concentrations of O_2 in gas phase are shown in Figure 3. When the potential was stepped from 0 to -0.9 V, the O_2 molecule in the supported $BMIPF_6$ membrane was reduced to $O_2^{-\bullet}$, and after several seconds the reduction current attained an approximately constant value, as a steady-state supply of O_2 from the gas phase into the membrane can be reached. In the reverse step (from -0.9 to 0 V), the current corresponding to the reoxidation of $O_2^{-\bullet}$ to O_2 was observed. Unlike the reduction current, the oxidation current gradually decreased and reached the background level after 20 s, because $O_2^{-\bullet}$ in the membrane was completely consumed. Thus, the transient and steady-state currents for the reduction of O_2 to $O_2^{-\bullet}$ ($I_{c,trans}$ and $I_{c,s}$ obtained at 0.4 and 20 s after the potential was stepped to -0.9 V) as well as the transient current corresponding to the reoxidation of $O_2^{-\bullet}$ to O_2 ($I_{a,trans}$ obtained at 0.4 s after the potential was stepped to 0 V) were typically used for measuring the concentration of O_2 in gas phase. The calibration curves (Figure 4) obtained for $I_{c,s}$ and $I_{c,trans}$ showed the straight lines with the sensitivities of 0.80 and 4.60 μA (% (v/v))$^{-1}$, respectively. The good linearity ($r^2 > 0.998$) of these two calibration curves obtained in the O_2 concentration range from 0 to 100% (v/v) demonstrates that this O_2 gas sensor has a wide detection range. The calibration curve obtained for $I_{a,trans}$ could be expressed by a quadratic equation, probably resulting from the limited diffusion of $O_2^{-\bullet}$ in the membrane and its decomposition. This point remains to be clarified theoretically. $I_{c,trans}$ response is recommended to use for O_2 sensing, as it is simpler to use a linear current-concentration relationship rather than a quadratic one, and in addition the $I_{c,trans}$ response is larger than the $I_{c,s}$ response. The utility of the present O_2 sensor is restricted for detecting O_2 in a dry gas stream. The sensor can be continuously used for at least twelve hours, and it can be easily recovered even if a water-containing sample gas should be flowed through the electrode system.

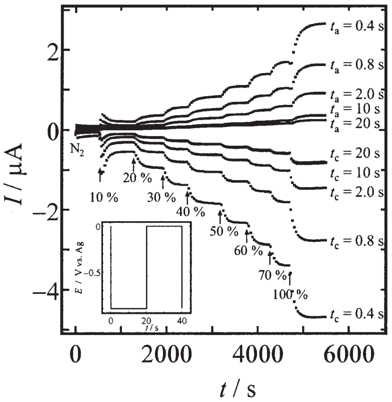

Figure 3. Typical potential-step chronoamperometric current responses obtained at the supported $BMIPF_6$ membrane-coated electrode in dried O_2 gas streams at 25 ± 1 °C. O_2 concentration was changed from 0 to 100% (v/v) O_2 in O_2–N_2 gas mixtures. The potential step was repeated between 0 and -0.9 V vs Ag every 20 s, shown as the inset. t_c and t_a mean the sampling times during the cathodic and anodic potential steps, respectively.

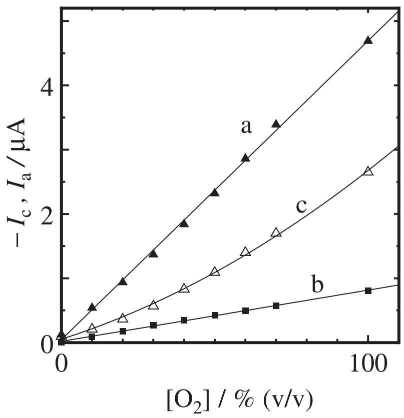

Figure 4. Variation of the current signal with O_2 concentration in O_2–N_2 gas mixed streams at the supported $BMIPF_6$ membrane-coated electrode. The data were obtained from Figure 3. The current responses were recorded at (a) t_c: 0.4 s, (b) t_c: 20 s, and (c) t_a: 0.4 s.

In conclusion, we have successfully developed an amperometric O_2 gas sensor based on the supported $BMIPF_6$ porous polyethylene membrane-coated electrodes. Some characteristic currents i.e., $I_{c,trans}$, $I_{c,s}$, and $I_{a,trans}$, obtained by potential-step chronoamperometry were used for determining the O_2 concentration in a dry gas stream. This sensor showed a wide detection range, a high sensitivity and a good reproducibility.

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