

# Ionic Liquids as Electrolytes for the Development of a Robust Amperometric Oxygen Sensor

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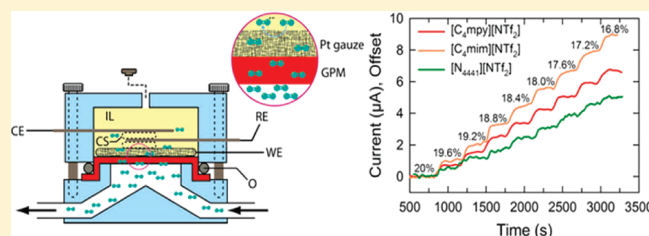
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**S** Supporting Information

**ABSTRACT:** A simple Clark-type online electrochemical cell design, consisting of a platinum gauze working electrode and incorporating ionic liquids (IL) as electrolytes, has been successfully applied for the amperometric sensing of oxygen. Studying ILs comprising the bis(trifluoromethylsulfonyl)imide anion, the obtained analytical parameters were found to be strongly dependent on the choice of cation. Compared with a conventional Clark cell design based on an aqueous supporting electrolyte, the modified oxygen sensor achieves substantial improvements in performance and stability. A limit of detection for oxygen as low as 0.05 vol %, linearity over an oxygen partial pressure between 0% and 20%, and a steady-state response time of 2 min was demonstrated, with a stable analytical response shown over the examined period of 90 days with no obvious fouling of the electrode surface. Based on the attractive physical attributes of ionic liquids (e.g., thermal stability beyond 150 °C), one can envision intriguing utility in nonstandard conditions and long-term online applications, as well as extension to the determination of other gases, such as methane and nitric oxide.



Several gas sensor technologies have matured to the point allowing their fairly noninvasive use in numerous aspects of our daily life (i.e., biomedical, safety, automotive). However, gas sensors that are stable and reliable with high sensitivity and selectivity, as well as being operable in harsh environments under low power with low operational costs, remain elusive, and they require significant innovation and advancement.<sup>1</sup> Thus, the development of robust and inexpensive gas sensors with minimal power requirements currently drives many researchers, including efforts within our laboratories. Among the common commercial gas sensor technologies (e.g., electrochemical,<sup>1b</sup> metal oxide semiconductive (MOS),<sup>2</sup> piezoelectric,<sup>3</sup> surface acoustic wave,<sup>4</sup> thermistor-based,<sup>5</sup> among others), electrochemical gas sensing remains among the most promising approaches to achieving the low power and low cost targets without sacrificing analytical performance, particularly in terms of sensitivity and selectivity.<sup>1a,6,7</sup> Electrochemical gas sensors are, in general, based upon measurement of changes in the properties of the electrode/electrolyte interface arising from interactions with gas analyte targets (e.g., O<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub>, SO<sub>2</sub>, ozone, formaldehyde). The two classical types of electrochemical gas sensor are the amperometric sensor and the potentiometric sensor, both of which have been successfully applied in commercial settings. Compared to potentiometric sensors, amperometric sensors exhibit high sensitivity, a wide detection range, and rapid response times, since they measure the current generated via redox reaction of an analyte at an electrode, either at a fixed or variable potential.<sup>1b</sup> Numerous

amperometric sensors have been developed over the past several decades to measure target gases such as oxygen and carbon dioxide.<sup>8</sup> These sensors display considerable variety in their design, most notably in electrode construction and choice of membrane, which significantly impacts size, cost, and performance (e.g., selectivity, sensitivity, stability). The electrolyte must also fulfill many requirements, including providing a medium for effective charge transport and contact at electrode surfaces and dissolution of reactant and product species to allow for efficient mass transport, while remaining (electro) chemically and physically stable under the conditions of sensor operation. Notably, the majority of gas sensors developed to date employ aqueous-based electrolytes which, although associated with highly charged and mobile carriers, suffer from solvent volatility, which can lead to exhaustion of the solvent in the reaction batch. Amperometric sensors using solid electrolytes (e.g., perfluorosulfonate<sup>9</sup> and Nafion ionomers<sup>10</sup>) have also been developed. Although solid-state electrolytes overcome problems of solvent loss/leakage from the sensor system, these electrolytes, by and large, cannot achieve sufficient room-temperature electrical conductivity due to a combination of insufficient electrical carriers and/or sluggish ionic mobility.

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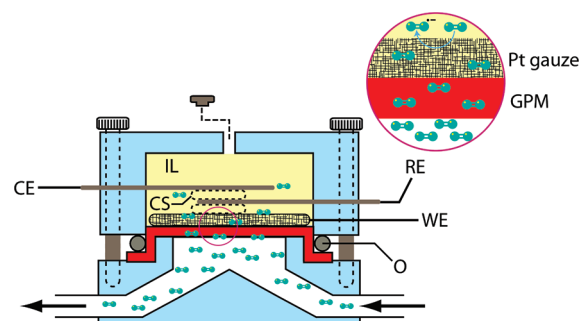
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The properties of the electrode/electrolyte interface often dictate the sensitivity, specificity, stability, and response time of a sensor. These analytical figures of merit critically define the success of an electrochemical detection technology from both technical and commercial viewpoints. Our laboratory has been working to develop next-generation electrochemical gas sensors that can be deployed in harsh/extreme environments by making use of room-temperature ionic liquids (RTILs) as the electrolytic medium. An ionically conductive fluid consisting of organic cations paired with a diversity of anions, ionic liquids (ILs) simultaneously enjoy benefits unique to both solid and liquid electrolytes.<sup>11</sup> For example, a host of ILs have immeasurably low vapor pressures at ambient temperature;<sup>12</sup> hence, evaporative loss of the electrolyte becomes a nonissue. Consequently, high stability and long lifetimes can be anticipated for gas sensors based on ILs.<sup>13</sup> Moreover, the low volatility of ILs has been shown to eliminate the need for a gas-permeable membrane in the sensor system,<sup>14</sup> simplifying device response since the diffusion layer no longer impinges upon a membrane. In addition, ILs frequently possess high thermal stability, which not only allows for facile sensor regeneration and decontamination, with favorable improvements in signal-to-noise (S/N) ratio, but also makes their use under nonstandard or extreme conditions (e.g., elevated temperatures, nonambient pressures) or in the presence of sensitive materials (e.g., controlled humidity environments in proximity to pyrophoric materials) an intriguing possibility. Finally, IL structural design and makeup can be carefully tuned to impart desired properties for nearly any application imaginable, making them excellent designer solvents for analytical chemistry in general.<sup>15</sup>

The determination of both gas phase and dissolved oxygen content has been of key interest for a period spanning more than 50 years, because of the importance in clinical diagnosis,<sup>16</sup> environmental monitoring,<sup>17</sup> industrial safety,<sup>18</sup> fuel cell technology,<sup>19</sup> and the automotive industry.<sup>20</sup> Oxygen sensors that can work in harsh environments, such as in underground mine warning systems or on-board automotive sensors for fuel efficiency monitoring, still require much improvement.<sup>21</sup> A handful of recent publications have described the electrochemical behavior of oxygen in ILs, intimating the potential in electrochemical oxygen sensing.<sup>22</sup> However, these studies have largely focused on investigation of the mechanism of oxygen reduction, offering insight into reoxidation processes, reactivity, stability, and electrochemical kinetics, with less focus given toward application and testing in real-world oxygen sensing applications. Studies on the electrochemical reduction of O<sub>2</sub> in imidazolium chloride–aluminum chloride molten salts were first initiated by Osteryoung and co-workers.<sup>23</sup> Al Nashef et al.<sup>24</sup> later reported on the reversible redox behavior of the oxygen/superoxide (O<sub>2</sub>/O<sub>2</sub><sup>•−</sup>) couple in [C<sub>4</sub>mim][PF<sub>6</sub>] solution. Recently, the Compton group determined the diffusion coefficient for O<sub>2</sub> and the formal redox potential and kinetic parameters of the O<sub>2</sub>/O<sub>2</sub><sup>•−</sup> redox couple in [C<sub>4</sub>mpy][NTf<sub>2</sub>], using membrane-free electrochemical cells.<sup>22b,25</sup>

Electrochemical sensors based on ILs frequently feature membrane-free electrochemical cells or microelectrodes, which show slow responses and small limiting currents, respectively, because of the relatively low conductivity manifested by the inherently high viscosity of ILs,<sup>26</sup> limiting their applicability in real-world scenarios.<sup>14b</sup> This arises because the gaseous analyte must diffuse through the IL electrolyte layer in order to reach the electrode surface where reduction can occur. This diffusional constraint is particularly apparent because typical ILs are ~50–200 times more



**Figure 1.** Side-view schematic diagram of Clark-type oxygen sensor designed around an IL electrolyte reservoir (not to scale). Figure abbreviations: CE, counter electrode; CS, cellulosic spacer; GPM, gas-permeable membrane; IL, ionic liquid; O, O-ring; RE, reference electrode; and WE, working electrode. Refer to the Experimental Section for details.

viscous than traditional aqueous electrolytes.<sup>27</sup> Assuming the Stokes–Einstein relation holds to a first approximation, this also implies that the O<sub>2</sub> diffusion coefficient in an IL can also be expected to be a few orders of magnitude smaller than that in water.

Classic Clark electrode designs consist of a sputtered or evaporated metal layer as the sensing cathode, deposited directly onto a thin gas-permeable membrane covering a layer of electrolyte. The membrane (frequently, polyethylene or a fluoropolymer such as poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) or poly(tetrafluoroethylene) (PTFE)) separates the internal electrolyte solution from the analyte matrix, preventing interference from nonvolatile electroactive components in the sample, and confining the oxygen diffusion to a finite region outside the cathode. Although this approach can potentially reduce the diffusional pathway for analyte, the so-formed electrode frequently exhibits poor conductivity. In order to marry the considerable advantages of IL-based electrolytes and amperometric Clark-type sensors, among other issues, a careful balance of conductivity and gas permeability must be considered.

The present paper reports on systematic studies of an innovative and easily fabricated Clark-type oxygen sensor based on an IL electrolyte layer immediately adjacent to a gas-permeable membrane. In the initial work, we established proof of concept for a sensitive IL-based amperometric Clark-type oxygen sensor that shows excellent long-term stability and reversibility. Subsequent experiments demonstrated the impact of changing the cation structure of the IL on the corresponding analytical parameters and studied sensor performance and selectivity under interfering conditions that include the presence of key electroactive species found in the atmosphere. The manifold benefits of ILs as electrolytes suggest great promise and generality for future generations of advanced and miniaturized electrochemical gas sensors seeking to meet stringent benchmarks in terms of cost, power requirements, robustness, sensitivity, and reliability for a host of demanding tasks, including high-temperature applications. In particular, it appears that use of a Clark membrane electrode design can largely overcome barriers introduced by the inherently high viscosities of ILs, empowering their use in developing other electrochemical gas sensors.

## EXPERIMENTAL SECTION

The ILs 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mpy][NTf<sub>2</sub>]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][NTf<sub>2</sub>]), tributylmethylammonium

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