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Ionic liquids combined with Pt-modified ordered mesoporous carbons as electrolytes for the oxygen sensing

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ABSTRACT

In recent years, room temperature ionic liquids (RTILs) have been highly utilized in electrochemical fields. Specifically, ionic liquids (ILs) as electrolytes augur promising potential for the next generation of advanced and miniaturized electrochemical gas sensors. In this paper, 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF_6]), 1-propyl-3-methylimidazolium hexafluorophosphate ([PMIM][PF_6]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) were synthesized through a facile one-pot method. We found that [EMIM][PF_6] and [PMIM][PF_6] exist in the solid state at room temperature. Hence, these ILs can effectively avoid the leakage of electrolytes. However, [BMIM][PF_6] can be present in liquid state at room temperature as the melting point decreases, due to the increasing of alkyl chain (C_n, $n < 6$) for the ILs. Compared to solid electrolyte gas sensors, sensors based on liquid electrolytes offer a reliable response and achieve sufficient ion mobility to sense oxygen. Our work provides an incentive to enhance the properties of a liquid electrolyte by mixing it with Pt-modified ordered mesoporous carbons (Pt-OMCs), which not only prevents the aggregation of OMCs but also provides a large number of active sites for oxygen reduction. The limit of detection (LOD) in oxygen sensors based on Pt/CMK-3-COOH-[BMIM][PF_6] is relatively low (1.10% O_2). Our results indicate that the synergistic combination of ILs and Pt-OMCs markedly promotes the performance of electrochemical oxygen sensors.

1. Introduction

Electrochemical oxygen sensors have been discussed widely in recent years [1]. The electrolyte is one of the significant components, which contacts all electrodes effectively and solubilizes the reactants and products for efficient mass transport. Therefore, electrolyte should be chemically and physically stable under all conditions of oxygen sensors operation [2]. One kind of well-known electrochemical gas sensors is based on a solid electrolyte, such as Ag_2SO_4 [3], ZrO_2 [4] and $ZnCr_2O_4$ [5]. However, the solid electrolytes show a low conductivity due to the combination of insufficient electrical carriers at room temperature, so oxygen sensors based on solid-state depend strongly on temperature [6,7]. Normally, these sensors are used at high temperature [8,9], resulting in large power consumption which is inconsistent with the contemporary needs [7,10]. However, using liquid electrolytes can result in the drying out of solutions and the inconvenience in fabrication and transportation of sensors. For example, acetonitrile, dimethylformamide and dimethylsulfoxide [11], which are traditional liquid electrolyte solutions, have been applied for various researches. In contrast to conventional electrolytes, ionic liquids (ILs) are preferable for manufacturing oxygen sensors, because of their wide electrochemical potential window, remarkable physical and chemical stability as well as excellent solubility for a range of materials. Moreover, one unique advantage is that the low vapor pressure of ILs can eliminate the need for a membrane and thus simplify sensor design [12–18]. Hence, the electrochemical gas sensors based on ILs tend to have a longer lifetime.

However, the majority of ILs-based electrolytes exist in the liquid state at room temperature. They have some disadvantages such as having a degree of fluidity, which limits their usage. As reported by Junqiao Lee et al. [19], 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([EMIM][NTf_2]) was incorporated with poly(methyl methacrylate) (PMMA), which improved

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the mechanical stability of [EMIM][NTf_2] and also reduced the impact from atmospheric impurities and moisture. However, the peak current and sensitivity of the oxygen sensor systematically decreased with the increasing content of PMMA. Thus we expect to improve the mechanical robustness of the electrochemical oxygen sensors by investigating ILs, which facilitates solid-liquid conversion by heating or cooling to meet the demand in certain situations, e.g. moving, shaking or tilting of the electrode, where loss of the ILs might occur [20].

Furthermore, the relatively low conductivity manifested by the inherently high viscosity of ILs and the comparatively small diffusion coefficients of gas molecules in ILs usually lead to slow responses and small limiting currents [21]. To solve these problems, great attempts are made to facilitate the diffusion of gas analytes in IL electrolytes. The most efficient strategy involves the formation of thin IL layers on microfabricated electrode arrays [22,23], which is expensive and could not be widely employed in the gas sensor field. This strategy produces IL layers with thicknesses up to several micrometers at the sensing interfaces and therefore effectively improves the performance of the IL-based sensors. However, it does not meet the rules of low cost and easy-to-use techniques of the contemporary society. So many researchers apply carbon nanotubes (CNTs)-modified electrolytes. Ming Zhou et al. [24] compared the responses of using OMCs and CNTs to modify glassy carbon electrodes for electrochemistry of eight kinds of materials. The study discovered that the OMCs-modified glassy carbon electrode has superior electron transfer kinetics in contrast to the CNTs-modified glassy carbon electrode. The OMCs exhibit a high specific surface area, a periodic mesoporous structure and chemical inertness, which make OMCs suitable for various of many applications including sensors [24–30]. The CMK-3, which is a type of OMC, possesses a marked ability to support ILs. To reduce the cost of sensors, the aggregation of Pt nanoparticles (NPs) should be avoided by being loaded on carbon supports. Therefore, Pt NPs were uniformly loaded onto the surface of CMK-3-COOH by the reduction of hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6{\cdot}6H_2O$).

Herein, we found that [EMIM][PF_6] and [PMIM][PF_6] can be present in solid state at room temperature but they easily melt after heating owing to their low melting points. Therefore, under the same high-temperature conditions, the ILs can be present in liquid state, which has higher electrical conductivity compared to solid electrolytes. The spill-less electrolytes are very robust for instability caused by moving, thus they possess portable application, avoiding a number of problems such as the leakage of liquid electrolytes. Hence, to a great extent, the lifetime of a gas sensor is prolonged and the field of application is broadened. Moreover, Pt/CMK-3-COOH is firstly introduced into imidazole-based ILs for detecting oxygen. An improved outcome is observed with a linear current response for oxygen reduction from 0 to 100% O_2. A sensor assembled with Pt/CMK-3-COOH and imidazole-based ILs exhibits outstanding gas sensing performance towards oxygen. This is ascribed to the large pore volume and specific surface area of CMK-3, which support Pt NPs for forming a porous composite. More importantly, the presence of Pt/CMK-3-COOH in the electrolyte accelerates the direct charge transportation in ILs [31–34].

Fig. 1. Scheme of preparation for Pt/CMK-3-COOH (a); Procedure of mixing Pt/CMK-3-COOH with [BMIM][PF_6] (b); Illustration of the structure of O_2 sensor (c).

2. Experimental section

2.1. Chemical reagents

ILs, 1-methylimidazole (Xiya Reagent), bromoethane (Tianjin Guangfu), 1-bromopropane (Aladdin Industrial) and 1-bromobutane (Xiya Reagent) were used directly without further purification. $H_2PtCl_6{\cdot}6H_2O$ and potassium hexafluorophosphate (KPF_6) were obtained from Xiya Reagent. The CMK-3 was supplied by XFNANO, INC, and sodium boronitride ($NaBH_4$) and silver nitrate ($AgNO_3$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile (MeCN, Sigma-Aldrich) solvent was used for washing the electrode before and after using with ILs. High purity N_2, 20% O_2, 40% O_2, 60% O_2, 80% O_2 and 100% O_2, which were purchased from Qinghua gases (Harbin, China) and used for electrochemical experiments.