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Impact of addition sheet-like cobalt in ionic liquids mixture to detect oxygen

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ABSTRACT

The incorporation of 1-alkyl-3-methylimidazolium hexafluorophosphate ($AMIMPF_6$) and 1-vinlyimidazole (VIM) firstly served as electrolyte for oxygen sensor, which remarkably promoted response current. Moreover, the sheet-like structure of cobalt was deposited onto the surface of C@TiC nanowire (Co/C), which endowed the imidazole-based ionic liquid electrolyte with plentiful active sites and fast electron transfer rate for oxygen reduction reaction. There was little literature about the integration of $AMIMPF_6$, VIM and Co/C as the electrolyte for oxygen sensor. The synergistic effect among all components was realized and maximized, leading to a superior performance of oxygen sensing compared to any component alone. The most important was that the composite material showed a fast response towards oxygen with an excellent linear relationship.

1. Introduction

In recent years, ionic liquids (ILs) have been utilized in many fields of biphasic catalysis, separation process and electrochemistry [1–4]. Furthermore, ILs have been recently used as sensing material for detection of oxygen [5]. ILs are entirely composed of ions and possess various attractive physical and chemical properties including negligible vapour pressure, wide electrochemical potential window and high solubility for a range of gases [6–11]. Compared with normal aqueous electrolytes, ILs are preferable for manufacturing oxygen sensors. Consequently, an admirable stability and a long lifetime can be expected for the gas sensors using ILs.

However, the relatively low conductivity of single IL leads to a tardy response and a weak response current [12]. One effective approach to overcome this deficiency is that alkenyl imidazole is incorporated into alkyl imidazole. It is well know that the mixture of unsaturated substituent and ILs can improve the conductivity of the sensor [13]. Well , the addition of Co/C can decrease response time for sensor, owing to it possessing plentiful active sites and outstanding electronic conductivity.

In this paper, our work focused on the fabrication of the composite electrolyte consisting of Co/C, $AMIMPF_6$ and VIM. And it was successfully applied for the preparation of electrochemical sensor with satisfactory result.

2. Experimental section

1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$), 1-propyl-3-methylimidazolium hexafluorophosphate ($PMIMPF_6$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) were synthesized through a facile one-pot method. Briefly, 0.10 mol 1-methylimidazole, 0.11 mol bromoalkane (bromoethane, 1-bromopropane or 1-bromobutane) and 0.11 mol KPF_6 were stirred for 3 h at 353 K in a flask, and then continuously rinsed with ultrapure water until no yellowish precipitate remained in the water layer, detecting with 0.5 mol L^{-1} $AgNO_3$ solution. The product was dried in a vacuum oven at 333 K for 24 h to remove moisture. The as-prepared samples were identified by FT-IR (Perkin Elmer Spectrum 100 Fourier transform infrared spectrometer) and ^1H NMR (Bruker Advance III-500 spectrometer) with deuterated dimethylsulfoxide. Then we mixed VIM with $BMIMPF_6$ in different mass proportions by ultrasonic processing.

According to cyclic voltammetry analysis, the optimal proportion was 40%$BMIMPF_6$+60%VIM. On this basis, the $BMIMPF_6$ was replaced by $PMIMPF_6$ or $EMIMPF_6$, and the conclusion demonstrated that 40%$EMIMPF_6$+60%VIM performed the highest redox peak response, the biggest conductivity and the fastest response. Meanwhile, the C@TiC nanowire arrays on Ti alloy substrate was prepared by Cui's method [14] and the modified substrate was immersed in the solution containing 1.00 mol L^{-1} NH_4Cl, 0.20 mol L^{-1} H_3BO_3 and 0.01 mol L^{-1} $CoCl_2{\cdot}6H_2O$. The electrodeposition of metallic cobalt was performed

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with the Autolab PGSTAT302 (Eco Chemie) electrochemical workstation in a conventional three electrode electrochemical cell with a saturated Ag/AgCl (3 mol L^{-1} KCl) reference electrode and a platinum foil counter electrode. The electrodeposition was carried out at a constant current of −5 mA for 1 h and the Co/C was collected by ultrasound from the TiC substrate. At last, we weighed a certain amount of Co/C to mix with $EMIMPF_6$ and VIM, and the mass proportions of Co/C, $EMIMPF_6$ and VIM were 5%, 38% and 57%, respectively.

The structures of the C@TiC and Co/C@TiC samples were characterized by X-ray diffraction (XRD, Rigaku TTR-III). And SEM images were obtained by scanning electron microscopy (SEM, Hitachi S-4800). Gas sensing properties were measured on a commercial CHI660E electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) by an interdigitated electrode, which is made of platinum (0.1 mm diameter). The impedance spectra obtained within 20% O_2 atmosphere were carried out at the open circuit potential. The other parameters of impedance spectra, the AC amplitude, initial frequency and final frequency, were set at ± 5 mV, 10^5 Hz and 0.1 Hz, respectively.

3. Results and discussion

The chemical structures and ^1H NMR spectrum of $AMIMPF_6$ are shown in Fig. S1. The Fig. S2 displays the XRD pattern and morphologies of as-prepared C@TiC and Co/C@TiC samples.

The performance of oxygen sensing in different mass proportions of $BMIMPF_6$ and VIM is investigated in Fig. 1a. By the force of contrast, the determined optimum mixing mass ratio is 40%$BMIMPF_6$+60% VIM. The response current value could reach −8.66 μA. Next, further experiments and electrochemical tests are showed in Fig. 1b-d. In contrast to 40%$BMIMPF_6$+60%VIM and 40%$PMIMPF_6$+60%VIM electrolytes, the 40%$EMIMPF_6$+60%VIM is preferable for manufacturing an oxygen sensor, because of its highest response current (−39.54 μA), shortest response time (9.5 s) as well as biggest conductivity (475.2 Ω).

Compared with the response current, response time and resistance in 40%$EMIMPF_6$+60%VIM electrolyte, the performance of oxygen sensing in 38%$EMIMPF_6$+57%VIM+5%Co/C electrolyte achieves substantial improvement (Fig. 2a-c). That is to say, remarkable activity and improved performance of oxygen sensing are observed. This reason is that the sheet-like structure of cobalt is very suitable for the electron transport during the electrochemical reaction process and results in an excellent performance.

The typical amperometric response curves of different scan rates and concentrations of O_2 are shown in Fig. 3**a** and **c**. A well-defined and stable amperometric response was gradually increased with enhancing scan rates and concentration of O_2, indicating highly efficient ability for O_2 electroreduction.

Fig. 3b shows that the corresponding plots of peak current vs. the square root of scan rate are linear, indicating that the reduction of oxygen is diffusion controlled. The relationship between the current values of the cathode peak and the concentration of O_2 is exhibited in Fig. 3d. The equation for the calibration curve is I=−43.91[O_2]−0.3373, where I/μA is the measured current and [O_2]/vol% is the oxygen concentration. The corresponding linear regression coefficient (R^2) value is 0.9995, and the limit of detection (LOD) is 2.30% and the sensitivity is obtained to be 43.91 μA (vol%)$^{-1}$, based on three times the standard deviation of the intercept. The relative standard deviation (RSD) is calculated to be 1.1%, 2.3%, 1.0%, 1.7% and 2.6% for 20%, 40%, 60%, 80% and 100% O_2, respectively. It absolutely demonstrates that 38%$EMIMPF_6$+57%VIM+5%Co/C can be used to manufacture oxygen sensor.

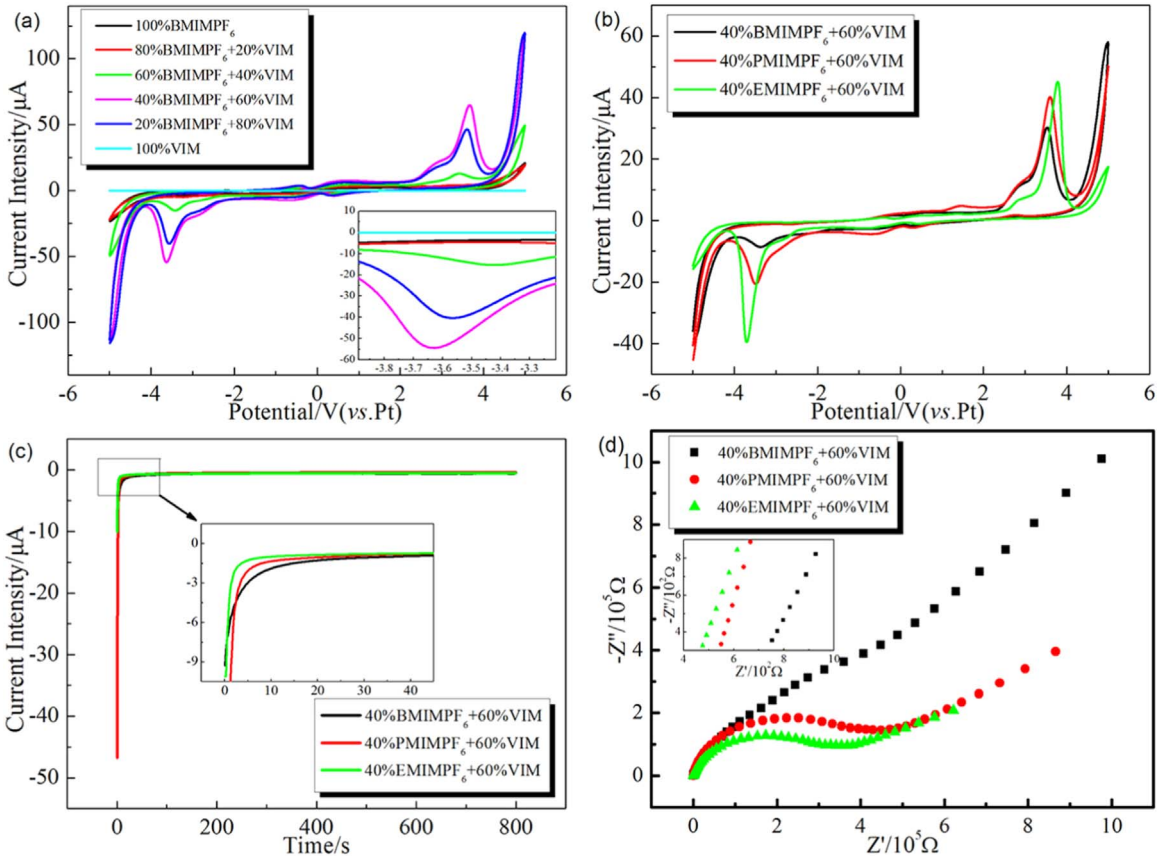

Fig. 1. The cyclic voltammograms in different mass proportions of $BMIMPF_6$ and VIM at scan rate 500 mV s^{-1} (a). The cyclic voltammograms in 40%$BMIMPF_6$+60%VIM, 40% $PMIMPF_6$+60%VIM and 40%$EMIMPF_6$+60%VIM at scan rate 500 mV s^{-1} (b), the chronoamperometric current curves in 40%$BMIMPF_6$+60%VIM, 40%$PMIMPF_6$+60%VIM and 40% $EMIMPF_6$+60%VIM at −2.0 V vs. Pt (c), the impedance spectra in 40%$BMIMPF_6$+60%VIM, 40%$PMIMPF_6$+60%VIM and 40%$EMIMPF_6$+60%VIM at open circuit voltage (d). Volume fraction of O_2: 20%. Temperature: 298 K.