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Electrochemical Behavior of Ionic Liquid Confined into Nanopores of Silica Gel Matrix

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Abstract: Imidazolium Ionic liquids (ILs) nano aggregates confined into nanopores of silica gel matrices (ILs-sg) modified electrodes were prepared by sol-gel process and characterized by cyclic voltammetry. Furthermore, the amounts of 15% ~ 28% ILs-sg and nano aggregates coated with ILs silica gel (ILs/sg) were prepared and their conductivities were evaluated by performing electrochemical AC impedance measurements from 20 °C to 80 °C. The abnormal results showed that, 1) comparing with the bulk IL, the confined IL had a positive shift effect of Fc/Fc^+ redox potential; 2) when IL confined into a nanospace, the electrochemical stability became poor; 3) the ion conductivity of ILs-sg was 29.6% ~ 136% higher than that of ILs coated silica gel, which could be attributed to the formation of nano ionic liquid network electrolyte. These results not only illustrate that the ILs based silica gel could serve as an excellent support of modified electrode for electrochemical active substance, but also reveal that the findings are helpful to understand the electrochemical phenomena of ILs under a confinement environment.

Key words: ionic liquids; silica gel; electrochemical behaviors; confinement effect

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Molecules tend to behave differently when placed in confined spaces. Confinement of molecules in nanoscale enclosures can result in drastic alterations in physical and chemical properties^[1-6]. Molecular level properties of confined fluids are of interest in many fields because of their importance in a variety of technological processes including catalysis, chromatography, materials, and membrane separations^[7-9].

Over the past decades, ionic liquids (ILs) have received increasing interest as alternative solvents and suitable soft materials in various applications^[10-11], and their properties such as negligible vapor pressure, low melting point, intrinsic ionic conductivity and high thermal stability make them possible to prepare confined ILs within nanoscale matrices and peculiar properties may exhibit. For example, it has been re-

ported that abnormal Raman spectra and enhanced or red shifted fluorescence of nano-confined ILs in mesoporous silica gel compared with bulk ILs were observed^[12-15]. The melting point of ILs confined in nanopores glass remarkably decreased in proportion to the inverse of the pore size and 1-butyl-3-methylimidazolium hexafluorophosphate confined in multiwalled carbon nanotubes possessed a high melting point^[16-18]. All these facts indicate that ILs confined with a nanoscale could exhibit very different physicochemical properties from bulk ILs, however, possible effects of their confinement into nanospace of materials on the electrochemical properties of ILs have not been studied yet. In this work, ILs confined into nanopores of silica gel matrices (ILs-sg) were characterized by cyclic voltammograms (CVs) and ion conductivity. We especially focused on the

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anomalous electrochemical behavior of ILs-sg different from that of the bulk ILs.

1 Experimental

All the chemicals used in the experiments were of analytical grade and used without further purification. 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF₆), 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm]BF₄), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIm]CF₃SO₃), and 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide (BMImNTf₂) were prepared carefully and purified rigorously in our laboratory with a two-step method according to literatures^[19-20], and their purity was confirmed by ion selective electrodes (halide content below 10 mg·L⁻¹). The halide free 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF₄) were prepared and purified according to the previous literature^[21]. All the ILs were dried and degassed under vacuum (ca. 10 mmHg) at 100 °C for 4 h prior to use.

1.1 Preparations of Silica Gel Confined ILs Modified Electrode (ILs-sg-ME), ILs-sg-ME Containing Electroactive Ferrocene (Fc-ILs-sg-ME), and Pure Silica Gel Modified Electrode (sg-ME)

The sol-gel stock solution was prepared by mixing 0.5 mL of tetraethyl orthosilicate (TEOS), 6 mL ethanol, 0.6 mL H₂O, 0.1 mL of 5 mmol·L⁻¹ NaOH, 0.5 mL 3.8% cetyltrimethylammonium bromide (CTAB) and 0.05 ~ 0.2 mL IL in a sealed conical flask at room temperature^[22]. Clear solutions were obtained after 3 h under magnetic stirring at room temperature and aged 1 h before use. The surfactant CTAB was added into the solution to prevent the sol-gel film on the electrode from fracturing. 1) For fabricating the ILs-sg-ME, 10 μL sol was pipetted to cover the surface of pre-cleaned GC, Pt, Au electrodes which were dried for ~ 5 h, and the IL content was 27% ~ 60%. 2) For the Fc-ILs-sg-MEs, ~ 50 mg Fc was additionally added to sol-gel stock solution of (1), ferrocene was dissolved into IL based sol to form

a nano microcosmic structure which encapsulated into this nano porous silica gel matrix. 10 μL sol was pipetted to cover the surface of pre-cleaned Pt, Au, and GC electrodes. 3) As for sg-MEs, the procedure was the same as the ILs-sg-MEs as long as the sol-gel stock solution was absent of IL.

1.2 Preparations of IL Confined Silica Gel, ILs-sg Matrix and Pure Silica Gel

The amounts of 0.2 ~ 0.5 g IL, 2.5 mL anhydrous ethanol, and 5 mL TEOS after distillation were mixed together and stirred at 40 °C for 2 h. Then the solution was added to 2.5 mL 38% (by mass) HCl solution dropwise under mild stirring in the ice water bath. The resultant mixed solution was continuously stirred at room temperature for 3 ~ 5 h, with the process of the sol-gel reaction of the silica, a colorless, transparent gel was obtained. And then the formed silica gel was treated under vacuum (40 mmHg) at 60 °C for 5 h to remove the solvent and the ethanol was produced from the sol-gel process. Furthermore, this silica gel was aged at 60 °C for 24 h. The transparent and small-block shaped solids with 15% ~ 28% ILs-sg were obtained and triturated for use. As for the pure silica gel, the synthesis procedure was the same as ILs-sg and only sol-gel stock solution was absent of IL.

The incorporated ILs were removed from ILs-sg by extraction method with the mixed solvent of acetone and ethanol (1:1, by volume), dichloromethane, respectively, under refluxing. The process was repeated for several times until the IL was completely removed, which was confirmed by a spectrum of the washed material measured with Fourier transform infrared spectroscopy (FT-IR). In order to prepare the ILs with the same loading of ILs/sg, the same amount of ILs was dissolved in 6 mL dichloromethane solvent, and the washed silica gel particulate was immersed, and then rotary evaporator was employed to ensure the homogeneous spread of the ILs onto the surface of the support under vacuum. The material was treated at 100 °C under vacuum (40 mmHg) for 5 h to remove the solvent and moisture to obtain ILs/sg for use.

1.3 Electrochemical and BET Measurements

Electrochemical measurements for CVs were performed using a CHI660A electrochemical workstation (CH Instruments, Austin, TX). The resistance of ILs based silica gel was evaluated by AC impedance spectroscopy. The electrochemical measurements were carried out in a N₂ filling equipment equipped with a chamber with which temperatures could be monitored and adjusted from room temperature to ca. 90 °C through a circular water bath system and vacuum treating (ca. 10 mmHg) to minimize the influences of O₂ and H₂O during the experiments. The working electrodes were bare Pt, Au, GC electrodes and ILs-sg-MEs, and the auxiliary electrode was a platinum wire. The reference electrode was a silver wire pseudo reference electrode or a saturated calomel electrode (SCE).

The conductivities of ILs-sg and ILs/sg were evaluated by electrochemical AC impedance spectroscopy in the range of 20 ~ 80 °C. The samples were dried for 5 h at 100 °C to remove physical absorbed water completely. The anhydrous IL-silica gel was sandwiched between two parallel mirror-finished stainless steel electrodes (area: 1.33 cm²) that were assembled in a Teflon holder to fabricate a "SS/IL-confined silica gel/SS" system, and this system was placed in the above-mentioned sealed vessel in which CVs were conducted. Impedance measurements were made with a 5 mV excitation signal over a frequency range of 100 kHz to 0.1 Hz, and the thickness of the gel was 45 μm. The point of intersection in an impedance spectrum between imaginary part and real part is the resistance (*R*) of samples, and the conductivity (σ) was evaluated by the following equation:

$$\sigma = L/(R \times S) \quad (1)$$

where *L* is the thickness of samples, and *S* is the area of samples. The N₂ adsorption measurements were done using a Micromeritics ASAP 2020 instrument to measure the surface area and porosity of silica gel using nitrogen at 77 K as the standard adsorptive gas. The surface area was obtained by the Brunauer-Emmett-Teller (BET) method and the pore size distribu-

tion was calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. The thermogravimetric analysis (TG) was conducted using a NETZSCH STA409PC thermal analyzer.

2 Results and Discussion

2.1 CV Studies of IL Confined into Nanospace

Electrochemical active ferrocene (Fc) was selected as a probe to study the electrochemical properties of ILs-sg-ME, and the CV curves are shown in Fig. 1. Different ferrocene contents and aging time were investigated and had a significant impact on the ferrocene redox behaviour. The electrochemical characteristics of this IL based silica gel matrix, which greatly depends upon the extent of cross-linking prior

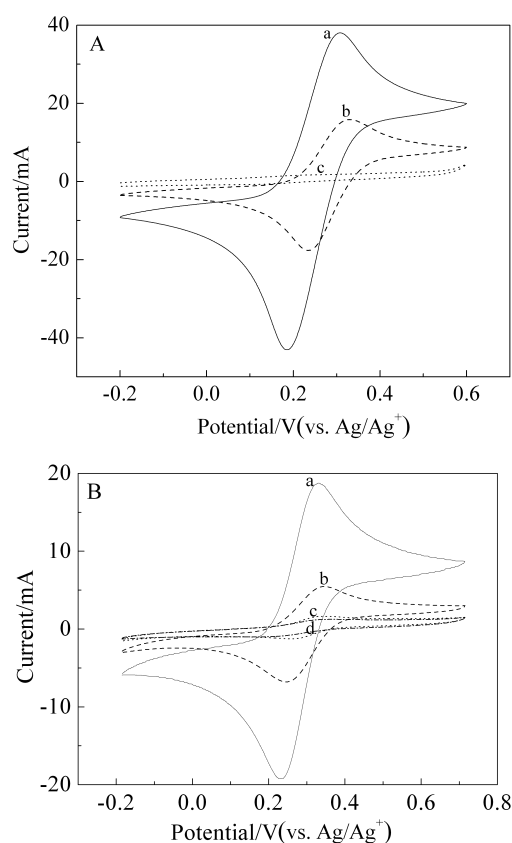


Fig. 1 A. Comparison in CVs of Fc-[BMIm]BF₄-sg-ME varied with Fc sol contents: 12.9 mg·mL⁻¹ (a), 8.6 mg·mL⁻¹ (b), 4.3 mg·mL⁻¹ (c), the aging time 1 h; B. Comparison in CVs of Fc-[BMIm]BF₄-sg-ME varied with different aging time, 1 h (a), 3 h (b), 5 h (c), 10 h (d), the Fc sol content 8.6 mg·mL⁻¹, scan rate = 50 mV·s⁻¹

to gelation, affects the diffusion of the doped species^[23]. Thus, the content of ferrocene and aging time must be considered. The ferrocene sol content and aging time were selected to be $8.6 \text{ mg} \cdot \text{mL}^{-1}$ and 1 h, respectively, in the following experiments.

To detect the different CVs behaviors of IL confined into nanopores of silica gel from bulk IL, a comparison in CVs of bare Pt electrode and Fc-ILs-sg-ME was studied. In the CV curve of bare Pt electrode [BMIm]BF₄ containing $10 \text{ mmol} \cdot \text{L}^{-1}$ ferrocene, see in Fig. 2a, the oxidation potential and reduction potential were 95 mV and 19 mV, respectively. As for Fc-[BMIm]BF₄-sg-ME, see in Fig. 2b, the Fc/Fc⁺ couple showed suppressed current peaks, and the oxidation potential and reduction potential became 317 mV and 197 mV, respectively. Compared with the bare Pt electrode in [BMIm]BF₄, the oxidation potential and reduction potential of Fc/Fc⁺ at Fc-[BMIm]BF₄-sg-ME were positively shifted 222 mV and 188 mV, respectively. Meanwhile, the ΔE_p (difference between oxidation potential and reduction potential) also increased from 76 mV to 120 mV. Additionally, for Fc-ILs-sg-ME, the ILs including [BMIm]BF₄, [EMIm]BF₄, [BMIm]NTf₂, [BMIm]PF₆, etc. and the electrodes including Pt, Au, GC, there was also a positive shift in the oxidation potential and reduction potential of Fc/Fc⁺, as well as an obvious increment of ΔE_p . All these indicated that the electrochemical

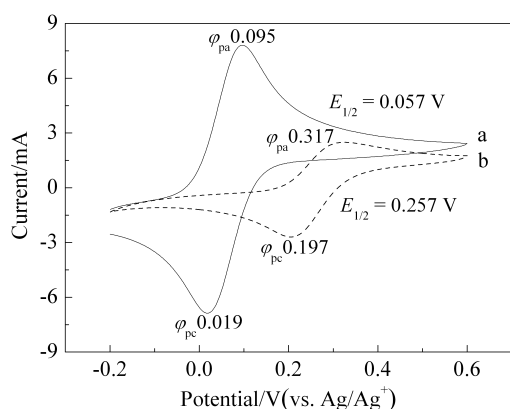


Fig. 2 CVs of Pt electrode in $10 \text{ mmol} \cdot \text{L}^{-1}$ ferrocene [BMIm]BF₄ (a) and Fc-[BMIm]BF₄-Pt-ME in [BMIm]BF₄ (b), scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, Ag wire pseudoreference electrode

property of IL when confined into a nanospace is much different from the bulk system. Although the detailed mechanism is not clear at this stage, it can be conjectured that the reason could be the confinement effect of IL confined into a nanospace or the interactional result of IL and silica gel.

Electrochemical window is often introduced to describe the electrochemical stability of ILs on a certain inert electrode. Herein, the electrochemical windows of ILs-sg-ME and bare GC electrode were compared to find the difference of ILs confined into nanopores of silica gel from bulk ILs. See in Fig. 3, comparing with the electrochemical window of [BMIm]PF₆ in bare GC electrode, not only the anodic limited potential but also cathodic limited potential moved to the zero potential. Because the confined [BMIm]PF₆ on modified electrode primarily was oxidized or reduced, the cathodic and anodic stabilities of encapsulated [BMIm]PF₆ were inferior to that of bulk [BMIm]PF₆, namely, the electrochemical stability of IL in a confined environment was decreased compared with that of the bulk IL. On the other hand, a new single irreversible oxidative peak at about -0.38 V was observed remarkably, this oxidative peak could be due to the oxidation of the substance c.a. carbene, through which the imidazolium cation was reduced^[24]. This reduced substance close to the surface of electrode was encapsulated into nanopores of silica gel and difficult to be diffused. It was easy to be oxidized, and these phenomena were present in some

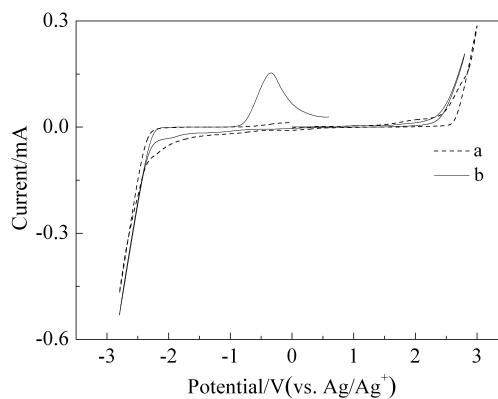


Fig. 3 CVs of bare GC electrode in [BMIm]PF₆ (a) and [BMIm]PF₆-sg-ME in [BMIm]PF₆ (b), scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, Ag wire pseudoreference electrode

Tab. 1 BET characterization of silica gel of ILS-sg after washing ILS (IL loading ~ 28%)

Ionic liquid	Average pore diameter/nm	Pore volume/(cm ³ ·g ⁻¹)	BET surface area/(m ² ·g ⁻¹)
[BMIm]BF ₄	10.1	1.11	343
[EMIm]BF ₄	5.5	0.72	451
[BMIm]PF ₆	10.2	0.86	386
[OMIm]BF ₄	11.1	1.15	329
[BMIm]NTf ₂	15.9	1.48	371
[BMIm]CF ₃ SO ₃	12.2	0.91	368

viscous ILS. Similar phenomena were also found in other ILS such as [BMIm]CF₃SO₃ and [BMIm]NTf₂ on Pt, Au, and GC electrodes.

2.2 Conductivity Studies of ILS-sg and ILS/sg

The ILS/sg was prepared by corresponding ILS-sg (~ 28% IL loading). The silica gel materials of ILS-sg after washing ILS were mesopores and displayed an average pore diameter of 5.5 ~ 12.9 nm, a pore volume of 0.72 ~ 1.48 cm³·g⁻¹ and surface area of 329 ~ 451 m²·g⁻¹ which was confirmed by BET (see Tab. 1). This suggested that varying the anion or the cation of the IL had a considerable effect on the pore structure of the silica gel.

The conductivity characterizations of ILS-sg and ILS/sg containing 15% ~ 28% (by mass) ILS such as [EMIm]BF₄, [BMIm]BF₄, [BMIm]PF₆, [OMIm]BF₄, [BMIm]CF₃SO₃, and [BMIm]NTf₂ were evaluated by AC impedance spectroscopy. The washing completeness of ILS-sg was confirmed by FT-IR spectroscopy. To confirm the reliability of the obtained results, we further performed the thermogravimetric analyses of ILS-sg and ILS/sg with a temperature range from room temperature to 400 °C, see Fig. 4. There was a negligible weight loss below 200 °C and the weight loss was less than 1% for all the samples in the investigated temperature range, which confirmed the negligible water influence on the conductivity of the samples.

The conductivities of ILS-sg and ILS/sg were studied by electrochemical AC impedance technique, see Fig. 5A. The conductivities of both ILS-sg and ILS/sg were below 2 × 10⁻³ mS·cm⁻¹, however, the conductivity of ILS-sg was 29.6% ~ 136% higher than

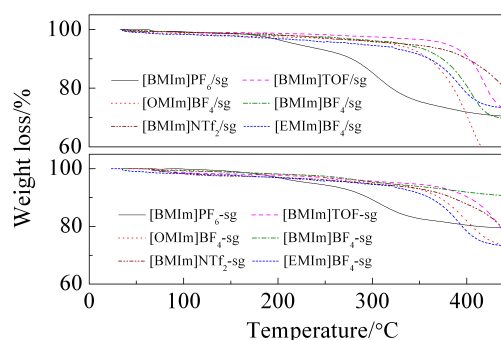


Fig. 4 Thermogravimetric curves of ILS-sg and ILS/sg with a temperature range from room temperature to 450 °C

that of ILS/sg with the same ILS loading at 20 °C. As for 15% [BMIm]BF₄-sg, the difference in conductivity became obvious when the IL content was in a comparatively low level, and if the IL content increased, this difference would diminish. This phenomenon could be due to the higher conductivity of ILS confined into nanopores than their surface conductivity of ILS coating on corresponding nanopores silica materials. The conductivities of all these materials decreased when elevating temperature from 20 °C to 80 °C, see Fig. 6B. This trend was reverse to the conductivity of IL or IL gel electrolyte reported^[8], and may be due to the ruleless Boulangé thermo-motion to hinder the ions movements of ILS-sg and ILS/sg.

3 Conclusions

In summary, the electrochemical properties of ILS-sg-ME and ILS-sg were characterized by CVs and conductivity measurements. The confined ILS had a positive shift and an obvious increment of ΔE_p for Fc/Fc⁺ redox couple. A new irreversible single oxidative peak was observed at ~ zero voltage (vs. Ag/Ag⁺)

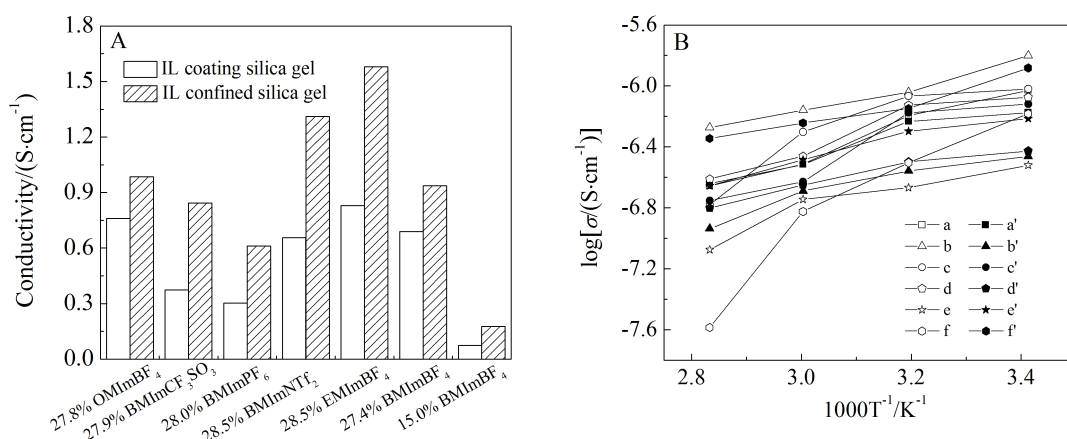


Fig. 5 A. Comparison in conductivities of ILs-sg and ILs/sg (the conductivity of pure silica gel is below $1.7 \times 10^{-3} \mu\text{S} \cdot \text{cm}^{-1}$); B. Comparison in conductivities of ILs-sg and ILs/sg for different temperatures (a, b, c, d, e, f refer to [BMIm]BF₄, [EMIm]BF₄, [OMIm]BF₄, [BMIm]CF₃SO₃, [BMIm]PF₆, [BMIm]NTf₂, X and X' refer to ILs-sg and ILs/sg, respectively)

on the ILs modified electrode in IL media, and was caused due to the oxidation of the slow-diffused substance in silica gel network through which the imidazolium cation was reduced. Comparing with the ILs coating silica gel, a higher ion conductivity was found for ILs-sg, which could be attributed to the formation of nano ionic liquid network electrolyte. These results not only illustrate that the ILs based silica gel could serve as an excellent support of modified electrode for electrochemical active substance, but also reveal that the findings are helpful to understand the electrochemical phenomena of ILs under a confinement environment. Further studies are under way.

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离子液体限域于硅胶纳米孔道中的电化学行为研究

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摘要: 通过溶胶-凝胶法制备了硅胶包载咪唑类离子液体修饰电极, 研究其与体相离子液体不同的伏安行为; 另一方面, 制备不同离子液体含量为 15%~28%的包载离子液体硅胶和涂覆离子液体硅胶, 用电化学阻抗研究其在 20 °C 到 80 °C 下电导率的变化情况. 异常的电化学行为主要表现在: 1) 硅胶包载离子液体导致 Fe/Fe⁺ 电对的半波电位正移 63.5~200 mV; 2) 当离子液体限域于硅胶纳米孔道中时, 离子液体的电化学稳定性变差; 3) 包载离子液体硅胶的电导率要比涂覆离子液体的电导率高 29.6%~136%. 由此推断, 可能是由于离子液体充满硅胶孔隙和孔道从而形成了纳米网状的离子液体导电介质. 这些结果表明, 硅胶包载离子液体不仅可以作为修饰电极的优良载体, 而且也有助于理解离子液体限域于硅胶纳米孔道中的限域效应.

关键词: 离子液体; 硅胶; 电化学行为; 限域效应