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Effect of Ionic Liquid Electrolyte on Electrochemical and Electrocatalytical Behaviours of Tri-Iron Cluster

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The tri-iron cluster, $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, has been reported as a catalysis to proton reduction at low overpotential. In this paper, the electrochemical behaviour of the tri-iron cluster and its catalytic effect on hydrogen evolution were investigated further by using ionic liquid (1-dodecane-3-methylimidazolium tetrafluoroborate, IL) as electrolyte in dichloromethane, considering that IL has unique chemical and physical properties. In contrast to the conventional electrolytes (such as $[NBu_4]BF_4$), the IL electrolyte increases the stability of the monoanionic radical generated from the first reduction and the electrocatalytic efficiency on proton reduction has also been improved.

Key Words: Ionic liquid, Electrochemistry, Electrocatalysis, Proton reduction, Iron carbonyl cluster.

INTRODUCTION

The need for novel energy sources as an alternatives to fossil fuels makes molecular hydrogen the ideal energy substituent in the future, which is no by-production. Efficient production of hydrogen has received considerable attention in the last decade due to the energy-related crisis. There are, however, few examples of efficient homogeneous catalysts for this reaction except for conventionally used precious metals. Since the revelation of the crystal structures of [Fe-Fe]-hydrogenase[1,2], many studies have been devoted to the synthesis and characterization of hydrogenase mimics containing di-iron core, $\{Fe_2S_2\}$-core, in which containing CO, CN^-, $-PR_3$ or an N-heterocyclic carbene[3-10]. Cyclic voltammograms have been widely used to investigate the behaviours of these mimics, with and without a source of protons. Mostly, electrolytes used in the cyclic voltammograms are traditional, such as $[NBu_4]BF_4$, $[NBu_4]PF_6$, $[NBu_4]CF_3SO_3$ and so on. But electrochemical studies have revealed that most of the mimic complexes are not stable, it is essential to improve these complexes stability as catalystes.

We recently studied that the electrochemical reduction of a tri-iron cluster, $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ (Fig. 1) exhibits a reversible reduction process involving one electron at -1.03 V and an irreversible reduction process at -1.75 V, the latter cathodic peak is attributed to the reduction of both transformation and the decomposed products from the first redox process[11]. Compared to the potential (*ca.* 1.9 V) for proton reduction without the presence of the complex, the improvement in over-potential is substantial, but the anion radical produced at the potential is instable in the solution of $[Bu_4N]BF_4$ as electrolyte[11,12], which prompted us to improve the stability of the catalysis of proton reduction.

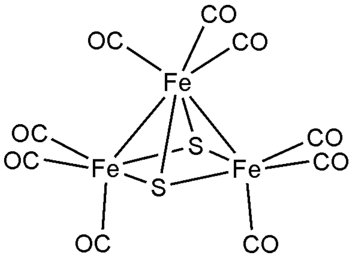

Fig. 1. Schematic structure of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$

Owing to 1-dodecane-3-methylimidazolium tetrafluoroborates (ILs) have unique chemical and physical properties, they have currently attracted much interests[13]. In electrochemistry, ILs show a broad electrochemical window of about 4.0 V and acceptable conductivity at *ca.* 10 mS/cm, which make them promising candidates as electrolytes[14].

In this paper, the synthesis, characterization of 1-dodecane-3-methylimidazolium tetrafluoroborate ($C_{12}MImBF_4$) and the electrochemistry and proton reduction catalyzed by the tri-iron cluster in the solution of this IL in dichloromethane are reported.

EXPERIMENTAL

Dichloromethane (DCM) for electrochemistry was purchased from Alfa Asear and freshly distilled over P_2O_5. In the purification of ionic liquid, non-aqueous solvents were purified by distillation and water was doubly distilled. Solutions used for electrochemical or spectroscopic analysis were prepared under an atmosphere of argon by using standard Schlenk technique. IR spectra were collected on Scimitar 2000 (Varian) FT-IR spectrophotometer.

Electrochemistry was carried out by using the same procedures as described elsewhere[15]. The concentration of the IL as electrolyte in electrocatalysis on proton reduction is 0.59 M. All potentials were quoted against ferrocenium/ferrocene couple. The tri-iron cluster, $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, was synthesized in the same procedure as described earlier[11].

Synthesis of 1-dodecane-3-methylimidazolium bromide ($C_{12}MImBr$): The method of preparation of 1-dodecane-3-methylimidazolium bromide was based on the method reported by literatures[16-18]. To a dry three-necked round-bottom flask, fitted with a reflux condenser and a thermometer, were added 1-methylimidazole (0.075 mol) and 1-bromododecane (0.085 mol), which were dissolved in heptanes (160 mL). The mixture was refluxed at 363 K overnight. Viscous and white gel was precipitated on the bottom of the flask and the solvent was removed under reduced pressure. The obtained viscous liquid was diluted with 25 mL of water, then it was washed with ethyl acetate (50 mL × 5), after which residual solvents were removed under reduced pressure for 2 days at room temperature. The product is colourless oily liquid at room temperature and ascertained by IR. IR (KBr, cm^{-1}): 1467 (m, sh), 1565 (m, sh), 2838(s, sh), 2915 (s, sh).

Synthesis of 1-dodecane-3-methylimidazolium tetrafluoroborate ($C_{12}MImBF_4$)[16-18]: A mixture of $C_{12}MImBr$ (0.075 mol) and $NaBF_4$ (0.10 mol) with 100 mL dry MeOH as solvent was stirred at 313 K for 48 h. When the metathesis was completed, white solid was removed from the mixture by filtration. The solvent of the filtrate was removed under reduced pressure to produce a sticky paste, which was further treated with dry dichloromethane. Any white solid formed was removed by filtration. Diethyl ether was added to the dichloromethane filtrate and viscous jelly was separated six times. The jelly-liked product was dried in vacuum for 48 h. Microanalysis for $C_{16}H_{31}N_2BF_4$ (338.24), found (calcd.) (%): C 56.75 (56.28), H 9.18 (9.24), N 8.33 (8.28). IR (KBr, cm^{-1}): 1061 (s), 1467 (m), 1565 (m), 2838(s), 2915 (s).

Electrical conductivity measurements: A low-frequency conductivity analyzer (model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy of ± 1 %) was used to measure the electrical conductivities of the solutions, which was calibrated with 0.01 M KCl solutions.

RESULTS AND DISCUSSION

Synthesis of $C_{12}MImBr$ and $C_{12}MImBF_4$: $C_{12}MImBr$ and $C_{12}MImBF_4$ were prepared by analogous literature producers[16,17]. As the product of $C_{12}mimBr$ is viscous liquid, which is not dissolved in ethyl acetate, some water was added to the liquid to lower its viscosity before purifying using ethyl acetate. $C_{12}MImBF_4$ was obtained from $C_{12}MImBr$ and $NaBF_4$ by metathesis. Considering that it is difficult to remove water from the product of $C_{12}MImBF_4$, anhydrous chloromethane and ether were used to purify the final product. The new featured peak of 1061 cm^{-1} of IR is attributed to the band of B-F in $C_{12}MImBF_4$.

Micelle formation of $C_{12}MImBF_4$ in dichloromethane: The specific conductivity (κ) of $C_{12}MImBF_4$ in dichloromethane is plotted against the concentration of $C_{12}MImBF_4$ at room temperature (Fig. 2). The value of κ increases linearly with the increase of the $C_{12}MImBF_4$ concentration and the slope changes abruptly at the concentration of 0.56 M. This abrupt change of the slope in the plot demonstrates that the molecular aggregates or micelles, start to form at the concentration corresponding to the break point[16,19-20]. The critical micelle concentration (CMC) derived from the break points in the κ *vs.* concentration plot is 0.56 M.

Cyclic voltammetry of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$: The IL is not active at the scanning scope (-0.60 ~ -2.0 V) of cyclic voltammogram with a glassy carbon electrode in dichloromethane at room temperature. Fig. 3 shows the cyclic voltammetry of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with different concentration of $C_{12}MImBF_4$. As shown in Fig. 3, the redox current of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ is steadily decreasing with the concentration

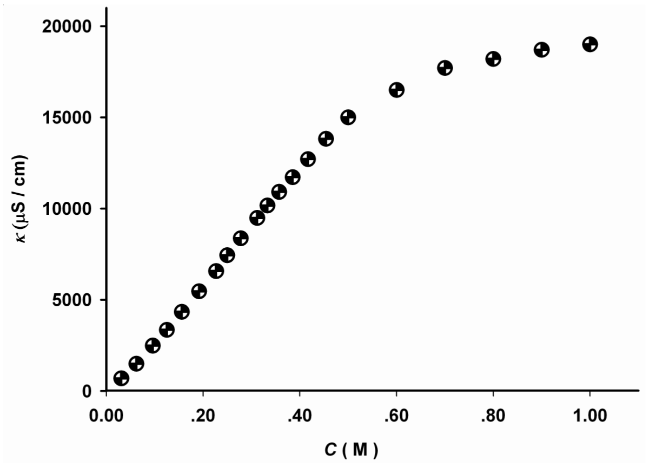

Fig. 2. Plot of specific conductivity, κ, against $C_{12}MImBF_4$ concentration, C, in dichloromethane at room temperature

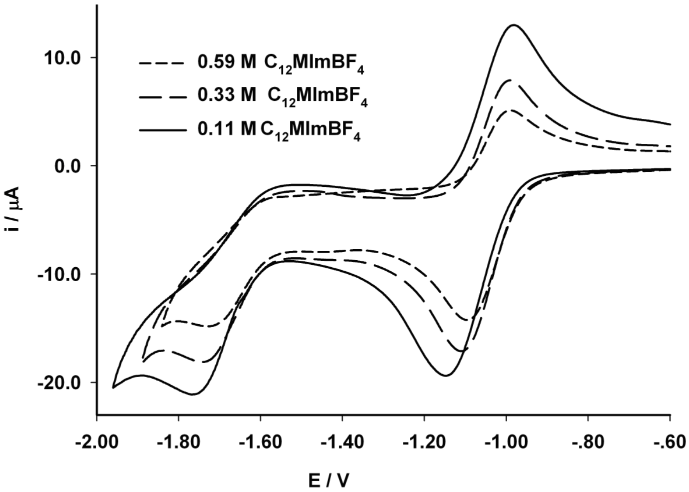

Fig. 3. CVs of 4.7 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with different concentration of $C_{12}MImBF_4$ in dichloromethane

of $C_{12}MImBF_4$. Figs. 4 and 5 show the difference of the activity of the tri-iron complex in $C_{12}MImBF_4$-dichloromethane and in $[NBu_4]BF_4$-dichloromethane and we can see that the current of the tri-iron in $C_{12}MImBF_4$-dichloromethane is weaker than in $[NBu_4]BF_4$-dichloromethane at the same condition, especially to the high concentration of $C_{12}MImBF_4$, the redox potential shifts negatively and the slop of the CV increases with the low concentration of the IL. In high concentration of $C_{12}MImBF_4$, the larger viscosity of the solution hinder the diffusion of ions and the lower diffusion cause the current decreased. The low concentration of the electrolyte in the solution leads the high resistance of the solution, which is attributed the increased slop and negative potential of the CV.

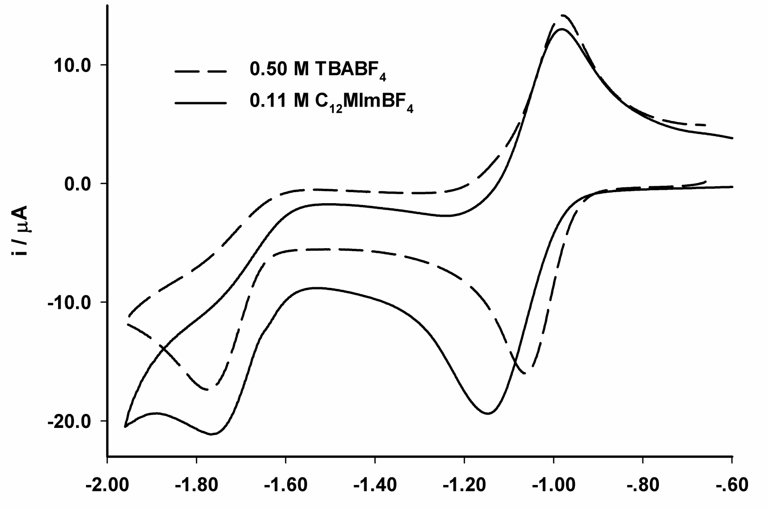

Fig. 4. CVs of 4.7 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with different electrolyte in dichloromethane

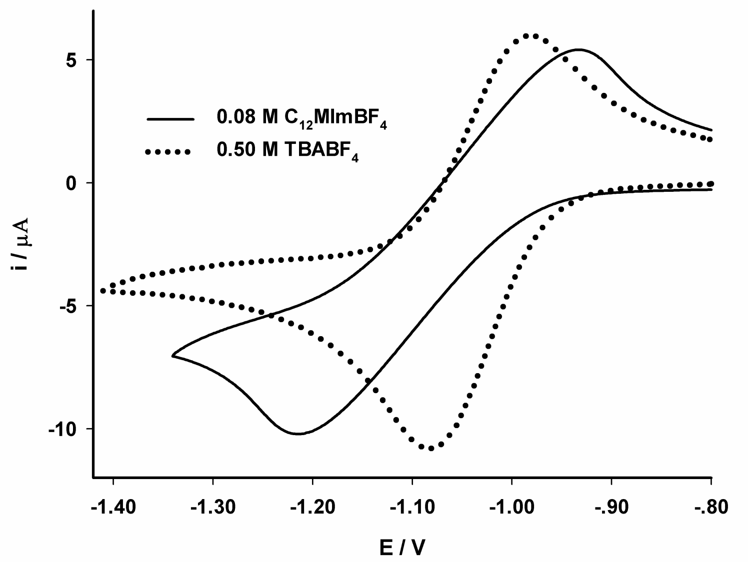

Fig. 5. CVs of 4.0 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with different electrolyte in dichloromethane

As be seen from previous studies[11] and the literature reported by Bockman and Kochi[12], the anionic radical originated at the first reduced step is unstable and the decomposition of the anionic radical involves CO loss and the decomposed products are oxided at -1.05 V, which indicate the anionic peak at -0.97 V is an overlap of peaks (Fig. 4, dotted line). Comparing the CV in $C_{12}MImBF_4$ to in $[NBu_4]BF_4$, the peak at -1.05 V disappear in the $C_{12}MImBF_4$ (Fig. 4, solid line). For the two peaks current ratio of the second (-1.73 V) and the first reduction (-1.03 V), it is about

0.65 in the solution of $C_{12}MImBF_4$ as electrolyte, which is smaller than the ratio of 0.73 in $[NBu_4]BF_4$-dichloromethane. The reversibility of the redox is improved in $C_{12}MImBF_4$-dichloromethane (Fig. 5). It is revealed that the intermediate of the tri-iron cluster, $[Fe_3(\mu_3\text{-}S)_2(CO)_9]^{\bullet-}$, is more stable in the solution containing ionic liquid than in $C_{12}MImBF_4$ solution. It is due to that $C_{12}MImBF_4$ is a surfactant and it is easy to form micelles in the solvent to suppress the decomposition[21].

Electrocatalytic activities of this tri-iron cluster towards hydrogen evolution in $C_{12}MImBF_4$-dichloromethane: In our previous work[11], we investigated the electrocatalytic activities of this tri-iron cluster towards hydrogen evolution in strong acidic media ($HBF_4·Et_2O$) in $[NBu_4]BF_4$-dichloromethane and its results show that the tri-iron cluster is a robust proton reduction catalyst,operating at a rather low over-potential (*ca.* 850 mV), but the anionic radical is not much stable. The purpose of improving the stability of the anionic radical inspired us to do further studies about the tri-iron cluster as a catalyst to proton reduction in the ionic liquid as electrolyte. Fig. 6 (left) involves the CVs low concentration (0.08 M) of $C_{12}MImBF_4$, as does high concentration (0.59 M) in Fig. 6 (right). In order to compare the catalytic behaviour to proton reduction using $C_{12}MImBF_4$ as electrolyte with $[NBu_4]BF_4$, the electrochemical catalytic behaviour was investigated to the amount of added acid (HBF_4) up to 15 equivalent (Fig. 7).

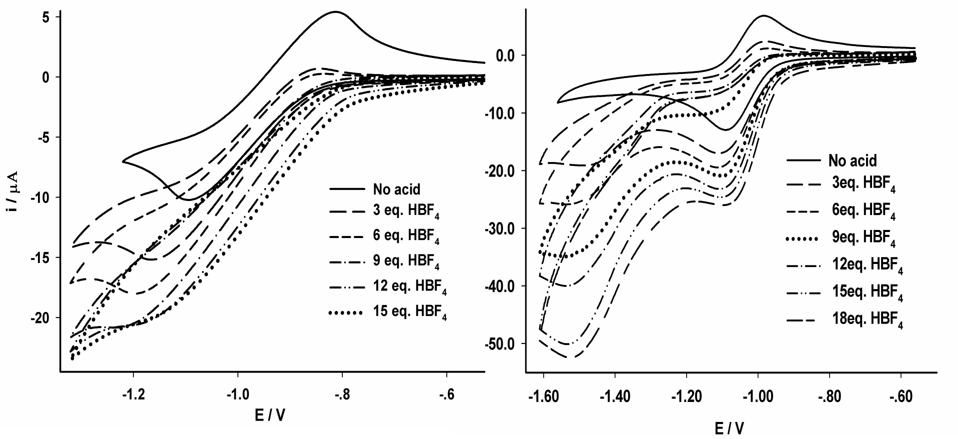

Fig. 6. CVs of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with different concentration of HBF_4 in the solution of $C_{12}MImBF_4$ in dichloromethane; Left: 4.0 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, 0.08 mM $C_{12}MImBF_4$; Right: 4.7 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, 0.59 mM $C_{12}MImBF_4$

As shown in Fig. 6(left), the current increases steadily till the acid is up to 9 equivalent and the maximum of the current is about 2.3 times of the parent complex in the solution of $C_{12}MImBF_4$, whereas is 1.9 times in $[NBu_4]BF_4$ as electrolyte (Fig. 7). It is more efficient using $C_{12}MImBF_4$ at low concentration than $[NBu_4]BF_4$, while at high concentration,the efficiency puts down. The potential shifts negatively using $C_{12}MImBF_4$ as electrolyte, it is also attributed to the high resistance in the solution.

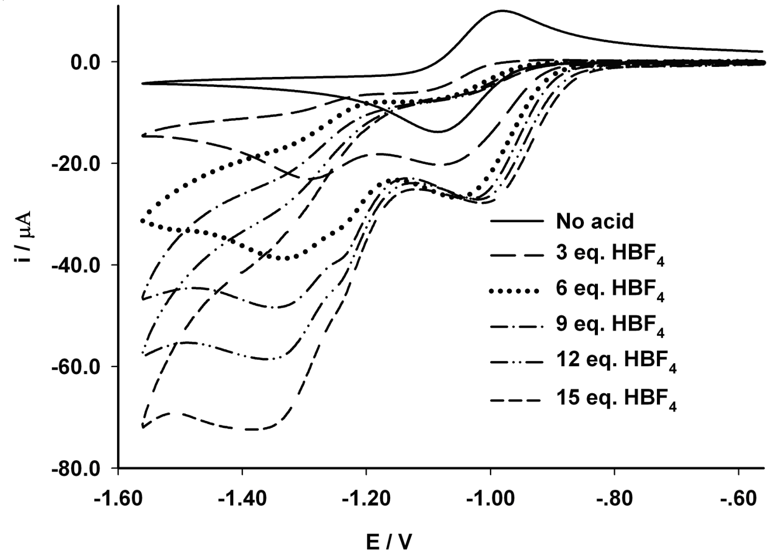

Fig. 7. CVs of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ (4.2 mM) with the different concentration of HBF_4 in 0.50 M $[NBu_4]BF_4$ in dichloromethane

Fig. 8 shows the CVs of 4.0 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with 15 equivalent in different concentration of $C_{12}MImBF_4$. As shown in Fig. 8, the current decreases steadily with the increasing amount of the IL, which is also associated to higher viscosity of the ionic liquid[17].

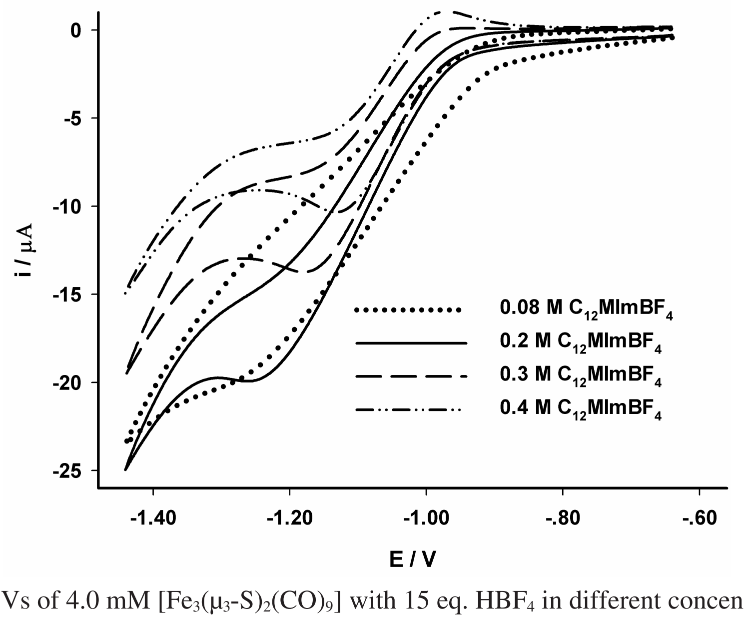

Fig. 8. CVs of 4.0 mM $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with 15 eq. HBF_4 in different concentration of $C_{12}MImBF_4$ in dichloromethane

Conclusion

In this paper, the electrochemical behaviour and electrocatalytic generation of dihydrogen using $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ with $C_{12}MImBF_4$ as electrolyte were further investigated. By comparing with that in normal electrolyte solution, $[NBu_4]BF_4$-dichloromethane, the results show that both the stability of the anionic radical generated at -1.03 V and the efficiency of catalytic proton reduction of the tri-iron complex using the IL as electrolyte are improved. It is demonstrated that the IL, $C_{12}MImBF_4$, is an ideal electrolyte for the electrochemical reaction of catalytic proton reduction by the tri-iron complex.

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