

Short Communication

Water Contained Ionic Liquid Medium for Electron Mediator Generation and its Quantification: A Paired Electrolysis Investigation**

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The present work aims to use ionic liquid as electrolyte medium to generate reductive electron mediator generation by paired electrolysis. The electrolytic cell potential analysis of 1-Butyl-3 Methyl imidazolium Trifluoromethane sulfonate [BMIM CF₃SO₃] ionic liquid with water content found minimum cell potential of 6.5 V found at 18 M water reveals paired electrolysis can be used in generation of electron mediators. Three different types of mediator precursors Ce(III)(SO₄)₂, [Co(II)(CN)₅]³⁻, and V(III)(acetylacetonate)₃ were underwent to generate reductive electron mediator by paired electrolysis. The quantification of reductive electron mediator by potentiometric titration with the help of H₂O₂ enables to reuse of the spent ionic liquid. Electrolytic reduction of V(III)(acetylacetonate)₃ metal complex in 18 M water contained BMIM CF₃SO₃ under optimized conditions reveals 65% of V(II)(acetylacetonate)₃ formation. A well-defined change in reduction efficiency of V(III)(acetylacetonate)₃ from 65 % to 15% upon addition of 20 mM dichloromethane demonstrates the dichloromethane reduction follows mediated electrochemical reaction (MER). The developed system facilitates to use ionic liquid in generation of electron mediator by paired electrolysis towards degradation of VOCs.

Keywords: Ionic liquid electrolyte, paired electrolysis, galvanostatic mode, electron mediator generation, VOCs

1. INTRODUCTION

The room temperature Ionic liquid (RTIL) has been considered as a green solvent due to its unique properties like inflammability, non-volatility, sustain to moisture and temperature [1]. Apart from its chemical synthesis applications [2,3], the RTILs have been introduced in to many electrochemical applications such as electrochemical sensors [4], battery [5], electrocatalytic process

[6], recovery of metal & metal polishing [7], and so on due to their wide electrochemical potential window than aqueous and non-aqueous solvents. Most of the electrochemical analysis of RTILs focused mainly on potential window identification with varying contents of solvents such as water [8], redox behavior of metal ions [9] and direct electrochemical oxidation/reduction of compound like H_2 [10], NO_2 [11] and CO_2 [12] etc., through the conventional potentiostat/galvanostat by three electrode system. Also, the RTIL has been used as an electrolyte medium to synthesis a specific intermediates or organic compounds [13-15] by using constant potential electrolysis with an idea of spent ionic liquids can be recovered and reused for the further electro-synthesis [16] in generation of specific organic intermediates of compounds. In other words constant current electrolysis has been ended up with high potential above 18 V [17] that high potential may dissolve any electrode (no study was reported) into the ionic liquid medium.

The Ionic liquids containing either hydrophilic or hydrophobic has a tendency to acquire atmospheric moisture and turns the IL's viscosity and density values with respect to moisture content [18]. On the other hand, the viscosity is directly propositional to the physical properties like conductivity and mass transportation of electrochemical active species that is advantageous for the electro-synthesis or electrochemical generation of active mediators [19]. With this idea, RTIL has been used as supporting electrolyte like TBAP, and CTAB in Volatile organic solvents and found enhances the charge transfer [20]. Instead of organic solvents, water also has been used and studied the redox behavior of Zn/Zn(II) in bmimntf2 and water mixture [21]. In presence of water and 1,2-dichloromethane, the ionic liquid tributylmethyl phosphonium methyl sulfate was analyzed through the redox behavior of ferrocenes [22]. Most importantly, the potential window shrinking effect took place depending upon the water content [8]. Advantageous of the potential window shrink can applied to use constant current electrolysis to generate redox mediators. Best of our literature knowledge, no constant current electrolysis was used to generate mediators especially for air pollutants degradation process.

In this present investigation, we have employed a galvanostatic method to generate mediator in water contained BMIM CF_3SO_3 using a paired electrolysis by Nafion324 membrane divided electrochemical cell. Initially, suitable reductive mediator was selected by paired electrolysis through oxidation/reduction potential (ORP) change. $Ce(III)(SO_4)_2$, $[Co(III)(CN)_5]^{3-}$, and $V(III)(acetylacetonate)_3$ precursors were tested to generate reductive mediators at cathodic half-cell. Quantification of the selected mediator was derived by potentiometric titration with H_2O_2 first time with the idea of reuse the ionic liquid. Further, different cathodes (Pt, Ag, Cu and graphite) and current densities were used to optimize effective generation of the selected mediator ion ($V(II)(acetylacetonate)_3$). Finally, the electrogenerated $V(II)(acetylacetonate)_3$ ($V(II)(acac)_3$) mediator was performed on dichloromethane (DCM) reduction and confirm by cyclic voltammetry (CV) analysis.

2. EXPERIMENTAL

2.1 Chemicals

The ionic liquid, 1-Butyl-3 Methyl imidazolium Trifluoromethane sulfonate [$BMIM^+ CF_3SO_3^-$]

99 % (purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China), Vanadium(III)(acetylacetonate)₃ (V(III)(acac)₃) 97% (Alfa Aesar), Cerium (III) sulfate octahydrate 99% (Samchun Pure Chemicals Co.Ltd). H₂O₂ 30 % (Daejung Chemicals and Metals .Co .Ltd) were purchased and used without further purification. The Ionic liquid mixture and Titrant have been prepared by using RO water with a resistance of 18Ω-cm. [Co(II)(CN)₅]³⁻ was prepared as in published literature [23] and used. In brief: 161.3 g potassium cyanide dissolved in 150 ml water (Caution! Potassium cyanide is highly toxic; proper care must be taken during handling) was added to cooled 160 ml of 120 g Co(NO₃)₂·6H₂O under nitrogen atmosphere (~ 6.2 cyanides per cobalt) and then an equal volume of chilled alcohol was added and the resulting mixture was slowly chilled until a mass of thin violet platelets appeared. The obtained cobalt cyanide complex sample was filtered rapidly and washed with cold alcohol then dried in a vacuum desiccator and stored in an air-tight brown bottle.

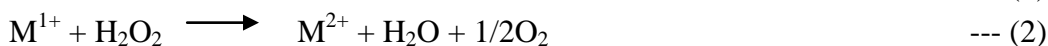
2.2. Electrolysis setup

The paired electrolysis setup was adopted as used elsewhere [24]. In brief, A 0.2 L solution of 20 mM mediator precursors in 18 M water contained BMIM CF₃SO₃ ionic liquid in water and 0.2 L of 18 M water contained BMIM CF₃SO₃ ionic liquid in water were placed in separate catholyte and anolyte tanks respectively. The anolyte and catholyte solutions were continuously circulated through the anode and cathode compartments of the electrochemical cell at constant flow rates (50 ml min⁻¹) using peristaltic pumps through a narrow gap of a divided cell (divided by Nafion[®]324 membrane). The reduction of mediator precursors was performed galvanostatically by applying different constant current densities between 10 to 50 mA cm⁻² using a DC power supply. The effective surface area of each electrode exposed to the solution was 4 cm². A mesh type Cu, Ag and Pt, and perforated graphite plate were used as electrodes in optimization studies.

CV experiments were performed custom made divided cell with Nafion324 membrane for working and counter electrodes. A platinum mesh and Ag wire were used as counter and quasi reference electrodes, respectively. Measurements were done with a PARC VersaSTAT 3 instrument.

2.3 Quantification of mediator

During the electrolysis, 2 ml of catholyte sample was collected and it was quantified by potentiometric titration. The initial oxidation/reduction potential (ORP) was negatively increased with electrolysis time that ORP value was bring back to its initial ORP value by titrating against 0.5 mM H₂O₂ solution. Using the consumed H₂O₂ volume, the electro-generated reductive electron mediator was quantified. The main role to use H₂O₂ is the spent ionic liquid can be reuse because the side product that obtained during quantification reaction is water [25,26], as shown eqns. 1 & 2.



3. RESULTS AND DISCUSSION:

3.1 Water content optimization

First, the divided electrochemical cell potential optimization with different concentration of water was derived by galvanostatic electrolysis (current density of 10 mA cm^{-2}) after 10 min or after static value attained and the results were shown in Fig.1. In presence of only ionic liquid, the cell potential showed 22 V, which is started decreasing with increasing water content to 6.5 V at water concentration of 18 M (Fig.1). Further addition of water causes a little decrease the cell voltage to 5.7 V and becomes almost constant in further addition explains the optimum water concentration is 18 M. The reason for the low cell potential at this 18 M water could be due to the stable emulsion structure formed between BMIM CF_3SO_3 and water [27] that could have led to less cell resistance. ~~The formed stable structure may dissociate if addition of more water concentration, which may be the reason for the increase in cell potential.~~ Thorough analyses will be needed to prove this hypothesis and this is away from the present focus. Thus, water concentration of 18 M in BMIM CF_3SO_3 medium was chosen for the further studies.

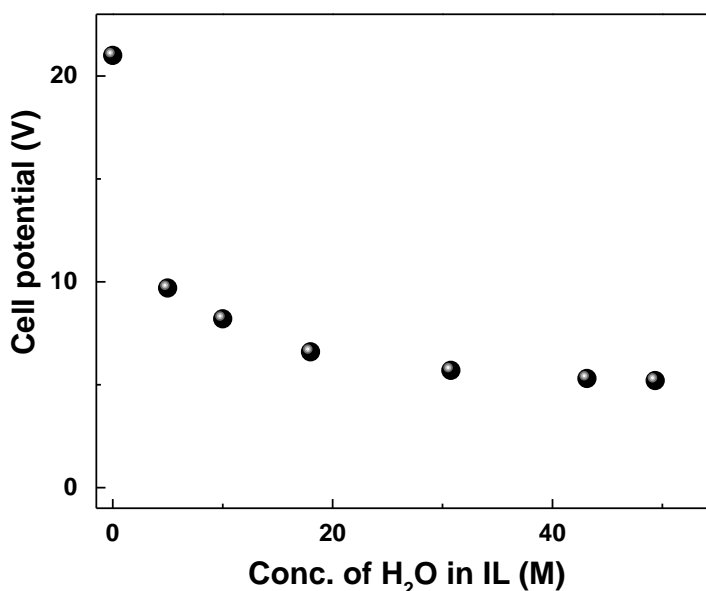


Figure 1. Cell potential variation on water addition into Ionic liquid BMIM CF_3SO_3 for the water concentration optimization. Conditions: Current density = 10 mA cm^{-2} Electrodes = Ti coated Pt (4 cm^2) as anode and cathode; Solution flow rate = 50 ml min^{-1} ; Electrolysis time = 10 min.

3.2 Mediator selection

Variation in oxidation/reduction potential (ORP) of the electrolyzed solution during electrolysis time is a key parameter in identification of the generation of a mediator, which is dissolved in the electrolyte medium. Fig.2 shows different ORP of different metal ions $\text{Ce(III)(SO}_4)_2$, $[\text{Co(II)(CN)}_5]^{3-}$

,and $V(III)(acac)_3$ during electrolysis in the cathodic half-cell by keeping only 18 M water contained BMIM CF_3SO_3 in water in the anodic half-cell. The $Ce(III)(SO_4)_2$ shows changes in ORP value from +340 mV to -115 mV in 10 min since then no abrupt change in ORP was noticed in further electrolysis time up to 1h, but maximum of -340 mV. Though a change in ORP value is shown, there appeared a pale gray color precipitate in 15 min. Note that the pH of the catholyte solution increased to 12 in 15 min, may due to water splitting due to the cell voltage 5.5 V, that could have made the $Ce(III)(SO_4)_2$ becomes precipitate by forming possible $Ce(III)(OH)_2$. Further, a $[Co(II)(CN)_5]^{3-}$ was attempted to electrolyze due to stabilization of low valent $[Co(I)(CN)_5]^{4-}$ formation [28]. Similar to $Ce(III)$, the initial ORP (+320 mV) for the $[Co(II)(CN)_5]^{3-}$ was decreased to -420 mV in 1h electrolysis with precipitate formation. According with Hanzlik and Vleck [28], the $[Co(I)(CN)_5]^{4-}$ formation will occur only above 4 M KOH solution. At the same time, $[Co(II)(CN)_5OH]^{3-}$ will be formed that is not soluble in the aqueous medium. Finally $V(III)(acac)_3$ was used as mediator in 18 M water contained BMIM CF_3SO_3 , the initial ORP value (50 mV) was reached slowly to -746 mV in 1h without any precipitate formation indicates the low valent $V(II)(acac)_3$ complex is soluble in the both the water contained BMIM CF_3SO_3 medium and stable as well. The insert figure of Fig.2 shows the $V(II)(acac)_3$ concentration variation during electrolysis that has been derived from the potentiometric titration with H_2O_2 . The $V(II)(acac)_3$ concentration found increased to 3 mM in the catholyte solution that is a scalable mediator. Worth to note it again that the advantages in the use of H_2O_2 in the potentiometric titration is the mediator precursor contained ionic liquid can be completely recovered because the side product formed during titration is water.

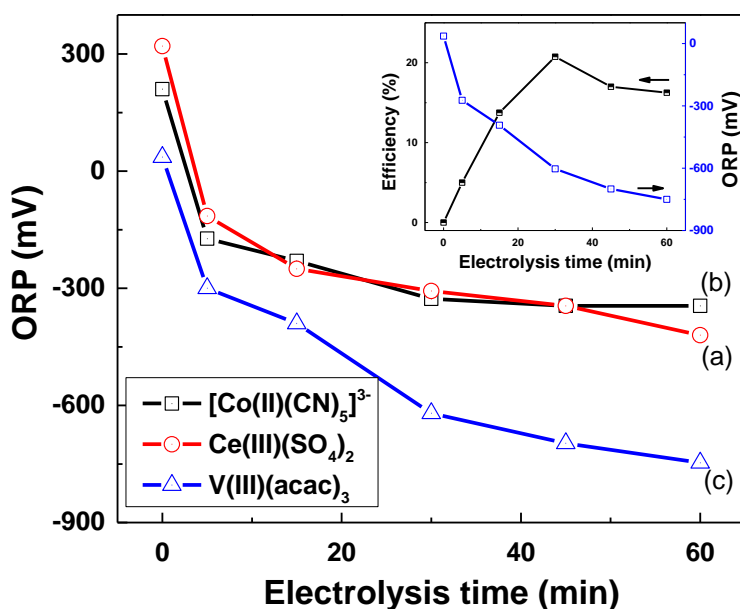


Figure 2. Oxidation/reduction potential (ORP) changes during electrolysis of different mediator precursors (mentioned in figure) in 18 M water contained BMIM CF_3SO_3 . Conditions: concentration of mediator precursors (10 mM); Cathode as Ag (4 cm²) and remaining conditions are same as in legend of Fig.1. Insert figure shows $V(II)(acac)_3$ formation with electrolysis time.

3.3 Effect of cathode and current density

The effect of cathode in the electrochemical generation of $V(II)(acac)_3$ in the 18 M water contained $BMIM\ CF_3SO_3$ was shown in the Fig.3. The reduction efficiency of $V(III)(acac)_3$ at all studied cathodes show almost same (12-14 %) up to 15 min, but varied in further electrolysis time. Especially, Copper electrode almost keep maintained between 11 to 9 %) the reduction efficiency in 1h duration. Pt and graphite cathodes further increased to nearly 20 % and then decreased to 16% and 18% respectively in 1h electrolysis time. In the case of Ag cathode, a maximum of 16% reduction efficiency reached and decreased to 13% in 1h electrolysis time. Although the $V(II)(acac)_3$ generation at the Pt and graphite cathodes found higher than the Ag and Cu, the cell potential for the graphite and Cu cathodes found to be 8.1 V and 8.4 V respectively, restrict to use due to possibility of high water splitting. At the same time Pt and Ag electrodes show cell potential of 6 V, which can minimize the side reactions such as water splitting, but Ag has been selected due to the less cost than Pt.

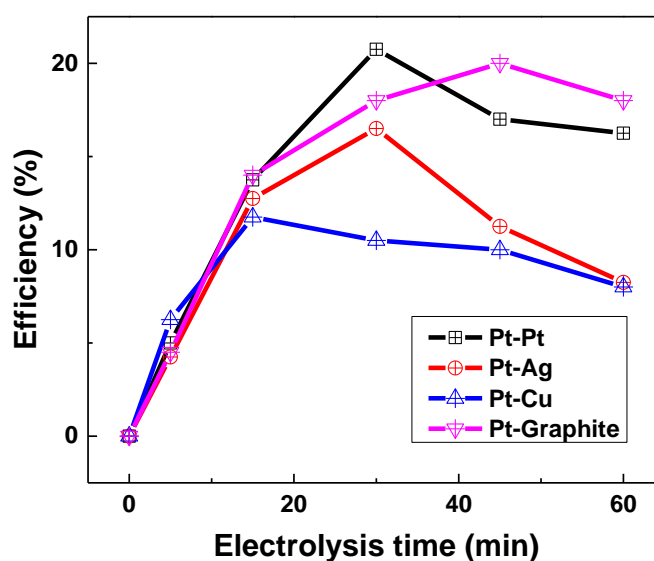


Figure 3. Effect of cathode variation (mentioned in the figure) on reduction efficiency of $V(III)(acac)_3$ during electrolysis in 18 M water contained $BMIMCF_3SO_3$. Remaining experimental conditions are same as in figure legend of Fig.1.

Further increase in current density on generation of $V(II)(acac)_3$ at Ag cathode leads higher generation efficiency as shown in Fig.4. At $15\ mA\ cm^{-2}$, the $V(II)(acac)_3$ generation is reached 20% in 25 min then decreased to 17% in 1h duration. At the same time, $25\ mA\ cm^{-2}$ shows nearly 30% generation efficiency in 15 min and keep maintained up to 1 h electrolysis time, which indicates the $V(II)(acac)_3$ generation is possible at higher current densities that means the rate of $V(II)(acac)_3$ formation is higher than the water splitting or overcome the water splitting.

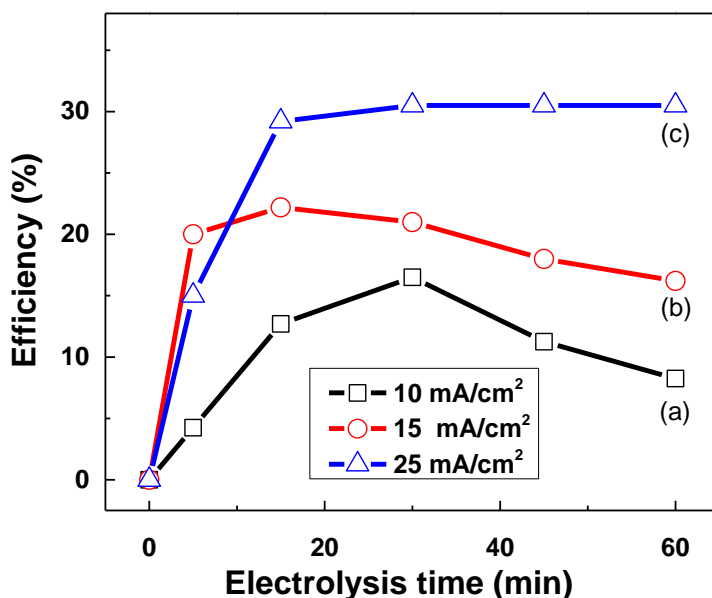


Figure 4. Current density variation (mentioned in the figure) on reduction efficiency of V(III)(acac)₃ in 18 M water contained BMIMCF₃SO₃ during electrolysis. Remaining experimental conditions are same as in the figure legend of Fig.2.

3.4 Electron mediator application

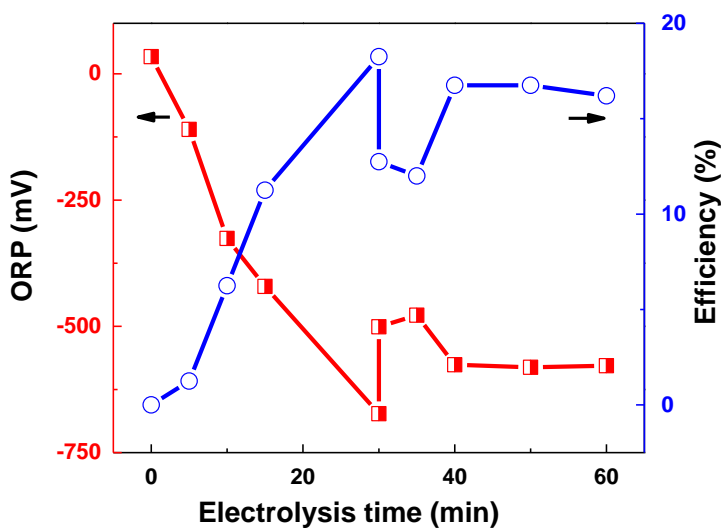


Figure 5. ORP and reduction efficiency variation of electrogenerated V(II)(acac)₃ upon additions of 20 mM DCM into electrolyzed solution of 18 M water contained BMIMCF₃SO₃. Remaining experimental conditions are same as in the figure legend of Fig.2.

Before addition the DCM, the V(II)(acac)₃ generation was reach nearly 60% and then 20 mM DCM was injected into the reactor for its degradation and the results are shown in Fig.5. Once 20 mM DCM is injected, the V(II)(acac)₃ concentration decreased to 6% and maintained around 7.2% up to 1 h reaction time (Figure 5 curve a). The ORP value also reduced to -540 mV from -750 mV and maintained throughout the reaction time (Figure 5 curve b) after addition of DCM. The reduction efficiency and ORP change during the addition of DCM concludes a reaction between V(II)(acac)₃ and DCM occurred in the reactor by the mediated electrochemical reduction (MER) process. Additionally,

CV experiments was carried out to support whether the DCM reduction follow MER process that are shown in figure 6. A cathodic reduction peak at -1.42 V is observed during forward scan with absence of corresponding anodic peak at reverse scan indicates V(III) reduction follow irreversible redox process. After the addition of 20 mM DCM, the V(III) cathodic reduction peak current is increased that clearly confirms the reduction of DCM follow MER process, which is typical of indirect electrocatalytic reduction process [29].

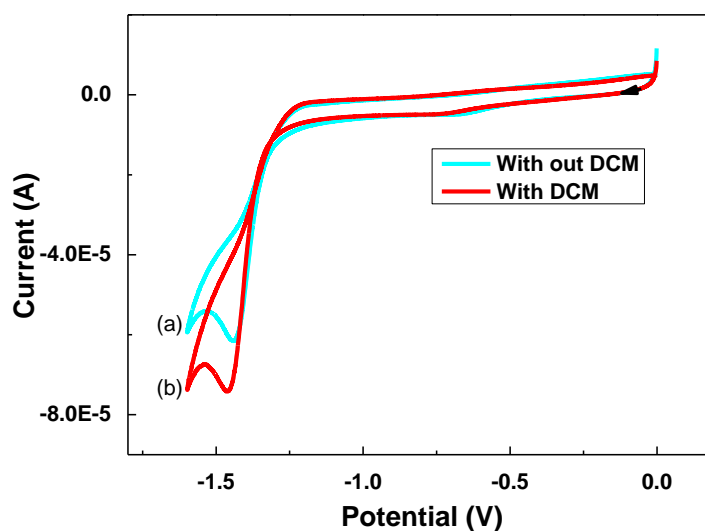


Figure 6. CV of V(III)(acac)₃ in 18 M water contained BMIMCF₃SO₃ in absence (a) and presence (b) of 20 mM DCM at scan rate of 50 mV/s.

4. CONCLUSIONS

The present investigation shown that water contained ionic liquid BMIM CF₃SO₃ is minimized the cell potential that alternatively allowed to use galvanostatic mode to generate reductive or oxidative mediators through paired electrolysis. The development of potentiometric titration with H₂O₂ confirms exact quantification of the electrogenerated mediator and paved a way to reuse the expensive ionic liquid. Through the water contents, electrode pair and current density, one can use the paired electrolysis using galvanostatic mode with enhanced generation efficiency. The developed 18 M water contained ionic liquid BMIM CF₃SO₃ with V(III)(acac)₃ was successfully applied to reduce a model compound DCM by galvanostatic paired electrolysis.

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