

Homogeneous reductive mediator generation using a water-containing ionic liquid medium by paired electrolysis for environmental pollutant degradation

G. Muthuraman, K.Kannan, And I. S. Moon*

Department of Chemical Engineering, Suncheon National University, #255 Jungangno, Suncheon 540-742, Jeollanam-do, Republic of Korea.

*corresponding author:

e-mail: ismoon@sunchon.ac.kr

Abstract. The aim of present work was to minimize the cell potential to generate a homogeneous mediator by constant current electrolysis towards air pollutant removal. Initial water content analysis with a 1-butyl-3 methyl imidazolium trifluoromethane sulfonate [BMIM CF₃SO₃] ionic liquid revealed a minimum cell potential of 6 V at 18 M water. Three types of mediator precursors, Ce(III)(SO₄)₂, [Co(II)(CN)₅]³⁻, and V(III)(acetylacetonate), were used to generate a reductive mediator by galvanostatic mode using paired electrolysis. The potentiometric titration with H₂O₂ enabled reuse of the spent ionic liquid after mediator quantification. The electrolytic reduction of V(III)(acetylacetonate) metal complex in 18 M water-containing BMIM CF₃SO₃ under optimized conditions revealed 65% of V(II)(acetylacetonate) formation. A well-defined change in the reduction efficiency of V(III)(acetylacetonate) from 18 % to 6% upon the addition of 20 mM dichloromethane demonstrated that dichloromethane reduction follows the mediated electrochemical reaction (MER). The developed system allows the use of galvanostatic mode to generate a mediator in an ionic liquid and the removal of VOCs in an effective manner.

Keywords: Water contained ionic liquid, paired electrolysis, galvanostatic mode, mediator generation, VOCs

1. Introduction

In the recent past, a room temperature ionic liquid (RTIL) is considered a green solvent owing to their unique properties, such as inflammability, non-volatility, sustain to moisture and temperature (Kato *et al.*, (2008)). In addition to its synthetic chemical applications (Reddy *et al.*, (2015); (Mehnert (2005)), RTILs have been introduced to many electrochemical applications, such as electrochemical sensors (Buzzeo *et al.*, (2004)), batteries (Ferrari *et al.*, (2009)), electrocatalytic process (Barhdadi *et al.*, (2009)), and recovery of metal & metal polishing (Serra *et al.*, (2014)). because of their wider electrochemical potential window than aqueous and non-aqueous solvents. Most electrochemical analysis of RTILs focused mainly on potential window identification with varying contents of

solvents, such as water (O'Mahony *et al.*, (2008)), redox behavior of metal ions (Xu *et al.*, (2013)), and direct electrochemical oxidation/reduction of compounds, such as H₂ (Silvester *et al.*, (2007)), NO₂ (Broder *et al.*, (2007)), and CO₂ (Li *et al.*, (2013)) etc., through the conventional potentiostatic/galvanostatic process using a three electrode system. In addition, the RTIL has been used as an electrolyte medium to synthesis specific intermediates or organic compounds (Yoshida *et al.*, (2008); Francke and Little (2014); Alvarez-Guerra *et al.*, (2015)) using constant potential electrolysis with the idea that spent ionic liquids can be recovered and reused for further electro-synthesis (Silvester and Compton (2006)) in the generation of specific organic intermediates of the compounds. In other words, constant current electrolysis has ended up with a high potential above 10 V (Xu *et al.*, (2014)) that may dissolve any electrode (no study has been reported) into the ionic liquid medium, which presents a new direction.

Ionic liquids, either hydrophilic or hydrophobic, have a tendency to absorb atmospheric moisture; the viscosity and density of an IL vary with the moisture content (Simons *et al.*, (2012)). On the other hand, the viscosity is directly proportional to the physical properties, such as conductivity and mass transportation of electrochemical active species, which is advantageous for electro-synthesis or the electrochemical generation of active mediators (Bornemann and Handy (2011)). With this idea, RTIL has been used as a supporting electrolyte, such as TBAP and CTAB, in volatile organic solvents that enhance charge transfer (Hapiot and Lagrost (2008)). Water has also been used instead of organic solvents, and the redox behavior of Zn/Zn(II) in a bmimntf2 and water mixture has been studied (Xu *et al.*, (2013)). In the presence of water and 1,2-dichloromethane, the ionic liquid, tributylmethyl phosphonium methyl sulfate, was analyzed through the redox behavior of ferrocenes (Stockmann and Ding (2015)). The potential window shrinking effect was dependent on the water content (O'Mahony *et al.*, (2008)). The advantages of the shrinking potential window can applied to constant current electrolysis to generate redox mediators. To the best of the authors' knowledge, no constant current electrolysis was used to generate mediators, particularly for the air pollutant degradation process.

This study investigated the galvanostatic method to generate a mediator in water containing BMIM CF₃SO₃ using paired electrolysis by a divided electrochemical cell. Initially, a suitable reductive mediator was selected by paired electrolysis through the change in oxidation/reduction potential (ORP). The Ce(III)(SO₄)₂, [Co(III)(CN)₅]³⁻, and V(III)(acetylacetonate) precursors were tested to generate reductive mediators at the cathodic half-cell. Quantification of the selected mediator was derived by a potentiometric titration with H₂O₂ for the first time with the idea of reusing the ionic liquid. Different cathodes (Pt, Ag, Cu and graphite) and current densities were used to optimize the effective generation of the selected mediator ion (V(II)(acetylacetonate)). Finally, the electrogenerated V(II)(acetylacetonate) (V(II)) mediator was performed on dichloromethane (DCM) reduction and confirmed by cyclic voltammetry (CV).

2. Experimental:

2.1 Materials

The ionic liquid, 1-butyl-3 methyl imidazolium trifluoromethane sulfonate [BMIM⁺ CF₃SO₃⁻] 99 % (purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China), Vanadium (III) acetylacetonate (V(III)), 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 as received. The ionic liquid mixture and titrant were prepared using RO water with a resistance of 18Ω-cm. [Co(II)(CN)₅]³⁻ was prepared as reported elsewhere (Adamson (1951)). Briefly, 161.3 g of potassium cyanide dissolved in 150 ml of water (Caution! Potassium cyanide is highly toxic; proper care must be taken during handling) was added to 160 ml of cooled 120 g Co(II)(NO₃)₂ under a nitrogen atmosphere (~ 6.2 cyanides per cobalt). An equal volume of chilled alcohol was then added and the resulting mixture was chilled slowly until thin violet platelets appeared. The cobalt cyanide complex sample obtained was filtered rapidly, washed with cold alcohol, dried in a vacuum desiccator and stored in an air-tight brown bottle.

2.2. Electrolysis setup

The schematic paired electrolysis setup used elsewhere was adopted (Govindan and Moon (2015)). Briefly, A 0.2 L solution of 20 mM Co(II)Cl₂ in 18 M water containing BMIM CF₃SO₃ ionic liquid and 0.2 L of 18 M water containing BMIM CF₃SO₃ ionic liquid were placed in separate anolyte and catholyte tanks respectively. The anolyte and catholyte solutions were circulated continuously through the anode and cathode compartments of the electrochemical cell at constant flow rates (50 ml min⁻¹) using peristaltic pumps through the narrow gap of a divided cell (divided by Nafion[®]324 membrane). The reduction of V(III) to V(II) 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 the electrodes in optimization studies.

CV was performed in a custom made divided cell with a Nafion324 membrane as the working and counter electrodes. A platinum mesh and Ag wire were used as the counter and quasi reference electrodes, respectively. The measurements were taken with a PARC VersaSTAT 3 instrument.

2.2 Quantification of mediator

During electrolysis, 2 ml of the catholyte sample was collected and quantified by potentiometric titration. The initial oxidation/reduction potential (ORP) was increased in the negative direction with increasing electrolysis time. The ORP value was returned to its initial ORP value by titrating against a 0.5 mM H₂O₂ solution. The electro-generated reductive mediator was quantified using the consumed H₂O₂ volume. The main reason for using H₂O₂ is the side product obtained during the quantification reaction, i.e., water (Kartasheva *et al.*, (2006); Cremasco and Mochi (2014)), as shown in eqns. 1 & 2, which will allow reuse of the spent ionic liquid medium after quantification of the electrogenerated mediator by evaporating the water.



3. Results and Discussion:

3.1 Optimization of water content

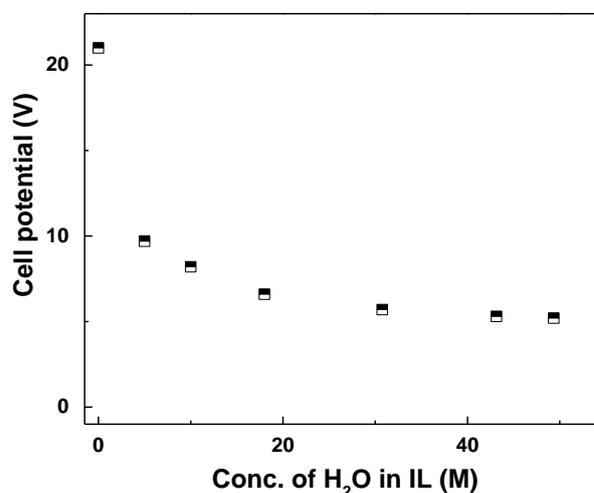


Fig.1 Cell potential variation upon water addition into ionic liquid BMIMCF₃SO₃ for the water concentration optimization. Conditions: Current density = 10 mAcm⁻² Electrodes = Ti coated Pt (4 cm²) as anode and cathode; Solution flow rate = 50 ml min⁻¹; Electrolysis time = 10 min.

The divided electrochemical cell potential with different concentrations of water was optimized by galvanostatic electrolysis (current density of 10 mA cm⁻²) after 10 min or after the static value was attained, as shown in Fig.1. In the presence of only ionic liquid, the cell potential was 18 V,

which began to decrease with increasing water content to 6.5 V at a water concentration of 3 M (Fig.1). Further addition of water caused a slight decrease in cell voltage to 5.7 V that became almost constant upon further addition, which explains why the optimal water concentration is 18 M. The low cell potential at this 18 M water could be due to the stable emulsion aggregation formed between BMIM CF₃SO₃ and water, which could have led to a lower cell resistance. The formed stable aggregation may dissociate under a higher water concentration, which may explain the increase in cell potential. Thorough analyses will be needed to prove this hypothesis but this is beyond the scope of the present study. Therefore, the water concentration of 18 M in a BMIM CF₃SO₃ medium was chosen for further study.

3.2 Selection of mediator

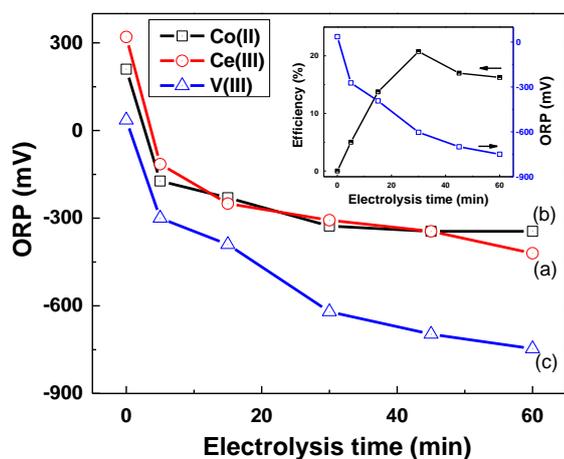


Fig.2 Oxidation/reduction potential (ORP) changes during the electrolysis of different mediator precursors (mentioned in figure) in 18 M water-containing BMIMCF₃SO₃. Conditions: concentration of mediator precursors (10 mM); Cathode as Ag (4 cm²) and remaining conditions are the same as in the legend of Fig.1. The inset figure shows V(II) formation with electrolysis time.

The variation in oxidation/reduction potential (ORP) of the electrolyzed solution during the electrolysis time is a key parameter in identifying the generation of a mediator, which is dissolved in the electrolyte medium. Fig.2 shows different ORP of different metal ions, Ce(III), Co(II), and V(III), during electrolysis in the cathodic half-cell by keeping only 18 M water-containing BMIM CF₃SO₃ in water in the anodic half-cell. The Ce(III) shows the changes in ORP value from +340 mV to -115 mV over a 10 min period because no abrupt change in ORP was noticed after further electrolysis time up to 1h; the maximum was -340 mV. Although a change in the ORP value was observed, there appeared a pale gray color precipitate in 15 min. Note that the pH of the catholyte solution increased to 12 within 15 min, which may be the result of water splitting because the cell voltage was 5.5 V, which could have made the Ce(III)(SO₄)₂ precipitate by forming Ce(III)(OH)₂. Furthermore, [Co(II)(CN)₅]³⁻ was used to electrolyze due to the stabilization of low valent [Co(I)(CN)₅]⁴⁻ formation (Hanzlik and Vlecek (1969)). Similar to Ce(III), the initial ORP (+320 mV) for [Co(II)(CN)₅]³⁻ decreased to -420 mV after 1h electrolysis

with precipitate formation. According to Hanzlik and Vlecek (1969), [Co(I)(CN)₅]⁴⁻ formation will occur only above a 4 M KOH solution. At the same time, [Co(II)(CN)₅OH]³⁻ will be formed, which insoluble in the aqueous medium. Finally, V(III) was used as a mediator in 18 M water containing BMIM CF₃SO₃, the initial ORP value (50 mV) slowly reached -746 mV in 1h without any precipitate formation, suggesting that the low valent V(II) complex is soluble and stable in the water-containing BMIM CF₃SO₃ medium. The insert in Fig.2 shows the V(II) concentration variation during electrolysis, which was derived from the potentiometric titration with H₂O₂. The V(II) concentration increased to 3 mM in the catholyte solution, which is a scalable mediator. The advantages in using H₂O₂ in the potentiometric titration is that the mediator precursor containing an ionic liquid can be recovered completely because the side product formed during titration is water.

3.3 Effect of cathode and current density

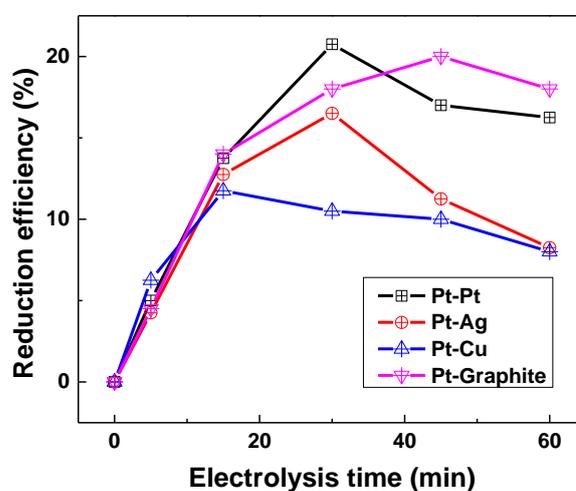


Fig.3 Effect of the cathode variation (mentioned in the figure) on the reduction efficiency of V(III)(acac) during electrolysis in 18 M water-containing BMIMCF₃SO₃. The remaining experimental conditions are the same, as in the figure legend of Fig.1.

Fig. 3 shows the effect of the cathode in the electrochemical generation of V(II) in the 18 M water containing BMIM CF₃SO₃. The reduction efficiencies of V(III) at all cathodes studied were similar (12-14 %) for up to 15 min, but varied with further increases in electrolysis time. In particular, The copper electrode was maintained a reduction efficiency between 11 to 9 % in 1h duration. The Pt and graphite cathodes increased further to almost 20 % and then decreased to 16% and 18%, respectively, after 1h electrolysis time. In the case of the Ag cathode, a maximum 16% reduction efficiency was reached, which decreased to 13% after 1h electrolysis. Although V(II) generation at the Pt and graphite cathodes was higher than the Ag and Cu, the cell potential for graphite and Cu cathodes was 8.1 V and 8.4 V, respectively, that may enhance possibly the high water splitting rate. At the same time, the Pt and Ag electrodes showed a cell potential of 6 V, which can minimize the side reactions, such as water splitting, but Ag was selected due to the less cost than Pt.

Further increases in current density on the generation of V(II) at the Ag cathode leads to higher generation efficiency, as shown in Fig.4. At 15 mA cm^{-2} , V(II) generation reached 20% in 25 min then decreased to 17% after 1h. At the same time, at 25 mA cm^{-2} , almost 30% generation efficiency was achieved in 15 min, which was maintained for up to 1 h electrolysis time. This indicates that V(II) generation is possible at higher current densities, which means the rate of V(II) formation was higher than the water splitting or water splitting had been overcome.

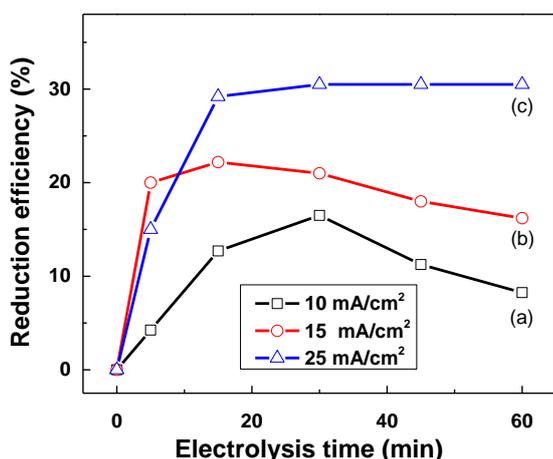


Fig.4 Current density variation (mentioned in the figure) on the reduction efficiency of V(III) in 18 M water-containing BMIMCF₃SO₃ during electrolysis. The remaining experimental conditions are the same as in the figure legend of Fig.2.

3.4 Application

Before the addition of DCM, V(II) generation reach nearly 18%. On the other hand, when 20 mM DCM was injected into the reactor for its degradation (Fig. 5), the V(II) concentration decreased to 6 % and was maintained around 7.2 % for up to 1 h reaction time (Figure 5 curve a). The ORP value also decreased to -540 mV from -750 mV and was maintained throughout the reaction time (Figure 5 curve b) after the addition of DCM. The reduction efficiency and change in ORP during the addition of DCM confirmed the reaction between V(II) and DCM by the mediated electrochemical reduction (MER) process. In addition, CV was carried out to determine if DCM reduction followed the MER process, as shown in figure 6. A cathodic reduction peak at -1.42 V was observed during the forward scan in the absence of a corresponding anodic peak at the reverse scan, which indicates that V(III) reduction follows an irreversible redox process. After adding 20 mM DCM, the V(III) cathodic reduction peak current increased, confirming that the reduction of DCM follows the MER process, which is typical of an indirect electrocatalytic reduction process [27 (Bard and Faulkner (2001))].

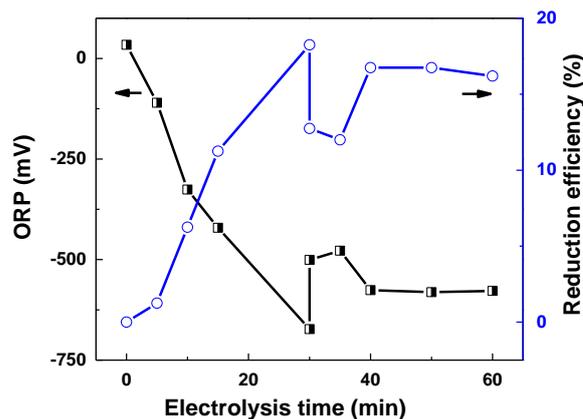


Fig.5 ORP and reduction efficiency variation of electrogenerated V(II) upon the addition of 20 mM DCM into the electrolyzed solution of 18 M water-containing BMIMCF₃SO₃. The remaining experimental conditions are same as in the legend of Fig.2.

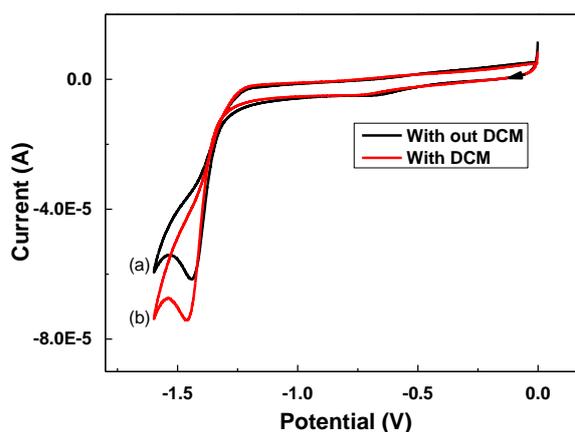


Fig.6 CV of 18 M water-containing BMIMCF₃SO₃ in the absence (a) and presence (b) of 20 mM DCM at a scan rate of 50 mV/s.

4. Conclusions

The present study showed that water-containing ionic liquid BMIM CF₃SO₃ minimized the cell potential that allowed the use of galvanostatic mode to generate reductive or oxidative mediators through paired electrolysis. The development of the potentiometric titration with H₂O₂ confirmed the precise quantification of the electrogenerated mediator and paves the way to reuse the expensive ionic liquid. Paired electrolysis using galvanostatic mode with enhanced generation efficiency

can be achieved by controlling the water content, electrode pair, and current density. The developed 18 M water-containing ionic liquid BMIM CF₃SO₃ with V(III) was applied successfully to reduce a model compound, DCM, by galvanostatic paired electrolysis.

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