



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Short Communication

2,2,6,6-Tetramethyl piperidine-1-oxyl mediated electrocatalytic oxidation of ethylene glycol in water and dichloromethane

Wenbin Zhang ^{a,b,*}, Zhixing Xiong ^a, Zhangcai Zhang ^a, Hang Gao ^a^a College of Chemistry and Bioengineering, Yichun University, Yichun 336000, China^b Engineering Center of Jiangxi University for Lithium Energy, Yichun University, Yichun 336000, China

ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form

1 October 2016

Accepted 24 November 2016

Available online xxx

Keywords:

TEMPO

Ethylene glycol

Carbonate buffer solution

Dichloromethane solution

Electrocatalytic oxidation

ABSTRACT

2,2,6,6-Tetramethylpiperidyl-N-oxyl (TEMPO) mediated electrocatalytic oxidation toward ethylene glycol was investigated as a function of electrolyte (aqueous carbonate buffer solution of pH 9.6 and dichloromethane solution with 2,6-lutidine as the base) by cyclic voltammetry and chronoamperometry. Both half-wave potentials and potential separations of electrochemical oxidation of TEMPO in these two electrolytes show differently. Electrocatalytic oxidation of ethylene glycol mediated by TEMPO was firstly reported here, it was observed the onset potential of this electrocatalytic oxidation reaction in dichloromethane solution is larger than that in carbonate buffer solution, moreover, electrocatalytic oxidation rate constant is calculated from chronoamperograms to be $1.63 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ in carbonate aqueous buffer solution, which is forty times as large as that in dichloromethane solution.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Electrocatalytic oxidation of alcohols to the corresponding carbonyl compounds is of importance due to its widespread applications such as organic electrosynthesis, energy storage, and electrochemical sensors [1–3]. The electrooxidation of ethylene glycol has attracted considerable interest due to its application in direct alcohol fuel cells and environment-friendly organic synthesis [4–8].

Generally, the redox mediator represents the key-element in successfully implementing an indirect electrocatalytic reaction, and because of their strong reactivity of hydrogen

abstraction, 2,2,6,6-tetramethylpiperidyl-N-oxyl (TEMPO) and its analogues have been widely used in the electrochemical oxidation of aliphatic, benzylic and allylic alcohols [9,10].

Several reactions of nitroxyl radicals mediated electrocatalytic oxidation toward alcohols have been examined, where many kinds of electrolyte solutions including alkaline aqueous electrolyte solutions [10–17], organic electrolyte solutions [18–21], organic solvent/water mixtures [16,17,22,23] and ionic liquids [21,24,25] can be used as reaction medias. Among them, in a 0.05 mol/L pH 9.6 carbonate buffer solution, 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (OH-TEMPO) was used as a mediator in the electrocatalytic oxidation of

* Corresponding author. College of Chemistry and Bioengineering, Yichun University, Yichun 336000, China.

E-mail address: zhangwbycu@163.com (W. Zhang).<http://dx.doi.org/10.1016/j.ijhydene.2016.11.165>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

vitamin B6 [11] and L-tyrosine [12] with glassy carbon electrode as a working electrode, the corresponding electrocatalytic apparent rate constants measured by chronoamperometry are $5.4 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $2.0 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively. Nitroxyl mixed self-assembled monolayers have been used for electrocatalytic oxidation of sec-phenethyl alcohol, where Tetrabutylammonium Hexafluorophosphate $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ was used as the electrolyte [18,19]. TEMPO mediated electrocatalytic oxidation of benzyl alcohol in acetonitrile solution was performed and its electrocatalytic rate constant was measured to be $5.53 \times 10^1 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ by chronoamperometry, where 2,6-lutidine is the base [21]. Besides the solvent of water and organic solvent, to ensure solubility of a wide range of alcohols in the electrocatalytic oxidation reaction medium, mixtures such as acetonitrile/water [16,17] and t-butanol/water [22,23] were employed as well.

Although many studies regarding nitroxyl radical mediated electrocatalytic oxidation of alcohols have been reported, electrocatalytic ability as a function of the electrolyte haven't been studied thoroughly, electron-transfer kinetics and catalytic rates of TEMPO mediated electrocatalytic oxidation of alcohols in acetonitrile and ionic liquids have been compared and it was concluded that, difference in viscosities induces the lower electrocatalytic ability in ionic liquids compared to acetonitrile [21,25]. To fully uncover the role of the electrolyte in the nitroxyl radicals mediated electrocatalytic oxidation of alcohol, in this work, two typical electrolyte solutions, one is 0.05 mol/L pH 9.6 carbonate buffer solution, the other is 0.05 mol/L $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ with 0.4 mol/L 2,6-lutidine as a base, were chosen as electrolyte solutions, and electrochemical behavior and catalytic ability of TEMPO mediated electrocatalytic oxidation of ethylene glycol in these two electrolyte solutions have been compared and discussed.

Experimental

Ethylene glycol, sodium carbonate, sodium bicarbonate, TEMPO, 2,6-lutidine, and dichloromethane were purchased from aladdin and used without further purification. All solutions were prepared freshly with deionized water (18.2 M Ω), A PHS-2F pH Meter (Shanghai REX Instrument, China) was utilized for measuring the solution pH. Both cyclic voltammetry and chronoamperometry were performed in CHI650E (CHI instrument, Shanghai, China) at room temperature with a standard three-electrode cell, a 3 mm diameter glassy carbon electrode was used as a working electrode, which needed to be polished and rinsed by deionized water before use, Ag/AgCl (saturated KCl solution) electrode was used as a reference electrode, and Pt plate was used as a counter electrode (all of three electrodes were purchased from Gaosunion, Wuhan, China).

Results and discussion

Cyclic voltammetry of TEMPO

It is well known that nitroxyl radicals can be electrochemically oxidized to form an corresponding oxoammonium species,

voltammograms of 1 mmol/L TEMPO at scan rate 100 mV/s in 0.05 mol/L pH 9.6 carbonate buffer solution and 0.05 mol/L $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2 + 0.4 \text{ mol/L}$ 2,6-lutidine were shown in Fig. 1, it is clearly to observe that half-wave potentials ($E_{1/2}$) of electrochemical oxidation of TEMPO are 548 mV and 721 mV, respectively. Manda measured half-wave potentials of electrochemical oxidation reaction of 3-Carbamoyl-PROXYL and OH-TEMPO when methanol, acetonitrile and water were used as solvents of electrolyte solutions [26], their results indicate that the half-wave potential is strongly dependent on the polarity of solvent, and $E_{1/2}$ decreases with the increasing of polarity. Considering that the polarity of dichloromethane and water are 3.4 and 10.2, respectively, the observed 173 mV negative shift of half-wave potentials from Fig. 1 may be ascribed to the stronger ion-dipole force between oxoammonium cations and solvent [27] in water over dichloromethane.

According to Randles–Sevcik equation:

$$i_p = 0.4463F^{1.5} \left(\frac{D}{RT} \right)^{0.5} A C_0 \nu^{0.5} \quad (1)$$

where i_p is the peak current, A is the surface area of a glassy carbon electrode, D is the diffusion constant of TEMPO and ν is the scan rate. Fig. 2a, b shows scan rate dependent voltammograms of 1 mmol/L TEMPO in dichloromethane solution and aqueous carbonate buffer solution, respectively, it is obviously that both the peak current and the peak separation increase with the increasing of the scan rate. Fig. 2c depicts the apparent linear fitting in plots of the square root of the scan rates $\nu^{1/2}$ versus the peak current i_p , which indicates that one-electron oxidation reactions of TEMPO in both dichloromethane solution and aqueous carbonate buffer solution are totally diffusion controlled. Based on Fig. 2c and Equation (1), diffusion constant of TEMPO in 0.05 mol/L pH 9.6 carbonate buffer solution was calculated to be $1.67 \times 10^{-5} \text{ cm}^2/\text{s}$, which close to that in 0.05 mol/L $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2 + 0.4 \text{ mol/L}$ 2,6-lutidine electrolyte solution ($1.60 \times 10^{-5} \text{ cm}^2/\text{s}$), it has been reported that diffusion constant of TEMPO in CH_3CN was measured to be $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$ by cyclic voltammetry [21].

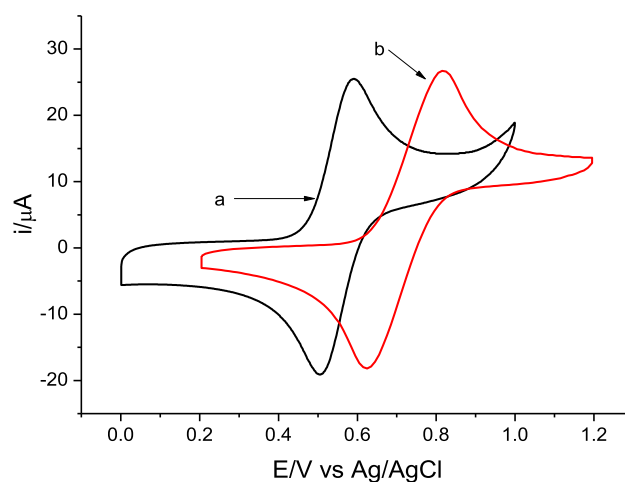


Fig. 1 – Cyclic voltammograms of 1 mmol/L TEMPO in (a) 0.05 mol/L pH 9.6 carbonate buffer solution (b) 0.05 mol/L $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2 + 0.4 \text{ mol/L}$ 2,6-lutidine.

Download English Version:

<https://daneshyari.com/en/article/5146510>

Download Persian Version:

<https://daneshyari.com/article/5146510>

[Daneshyari.com](https://daneshyari.com)