

Electrochemical desorption of a self-assembled monolayer of alkanethiol in ionic liquids

Daisuke Oyamatsu^a, Takeshi Fujita^a, Satoshi Arimoto^{a,b}, Hirokazu Munakata^a, Hajime Matsumoto^c, Susumu Kuwabata^{a,b,*}

^a Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 5650871, Japan

^b CREST, JST, Kawaguchi, Saitama 3320012, Japan

^c Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 5638577, Japan

Received 17 July 2007; received in revised form 28 November 2007; accepted 4 December 2007

Available online 8 December 2007

Abstract

Electrochemical desorption of a self-assembled monolayer (SAM) of *n*-alkanethiols was investigated in four kinds of ionic liquids. It was found for the first time by linear potential sweep voltammetry that reductive desorption of the SAM took place even in ionic liquids. The potential peak was negatively shifted with an increase in the alkyl chain length of the alkanethiol SAM in a manner similar to that for the case of reductive desorption of the SAM in an aqueous solution. However, the cathodic wave broadened with an increase in chain length, although its width became narrow in the case of measurements in an aqueous solution. The contrary behaviors of reductive desorption in an ionic liquid and in an aqueous solution were discussed by comparing the experimentally obtained voltammograms with numerically simulated ones. Based on the results obtained, we propose a plausible reaction scheme in which cations work mainly as charge compensators for generated alkanethiolates and anions work as a solvent.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Self-assembled monolayer; Reductive desorption; Alkanethiol; Ionic liquid; Numerical simulation

1. Introduction

Ionic liquid, which is a room temperature molten salt, is receiving considerable attention in various chemical fields because of its remarkable features such as non-volatility, non-combustibility, high ionic conductivity and capability to dissolve many kinds of substances [1–8]. In the electrochemical field, measurements of electrochemically active species in ionic liquid, including simple redox reaction of ferrocene derivatives, have revealed that ionic liquid is utilizable well as an electrolyte [9–12]. Attempts have, therefore, been made to apply this non-volatile electrolyte to

electrochemical devices such as lithium ion batteries [13–17], fuel cells [18,19], and solar batteries [20–22]. However, its property as an electrolyte has not yet been completely elucidated because an electrolyte without any solvent has not been considered in conventional theories of electrochemistry. Therefore, further studies are required to completely understand the roles of anion and cation of the ionic liquid as an electrolyte.

A self-assembled monolayer (SAM) of *n*-alkanethiol formed on a metal substrate (Au, Pt, or Cu) has been intensively studied since publication of the first report by Allara and Nuzzo in 1983 [23]. The SAM possesses sufficient stability due to its highly organized structure developed by van der Waals forces between alkyl chains. However, as reported first by Porter et al. [24], the closely packed monolayer can easily be desorbed by electrochemical reduction formulated by

* Corresponding author. Address: Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 5650871, Japan. Tel./fax: +81 6 6879 7372.

E-mail address: kuwabata@chem.eng.osaka-u.ac.jp (S. Kuwabata).



where R and M represent an alkyl chain and a metal electrode, respectively. This reaction gives a definite cathodic wave in linear sweep voltammetry of the SAM-coated electrode in an aqueous electrolyte solution, and its shape and peak potential are sensitive to several parameters, including length of the alkyl chain, kind of substituted functional group, and kind of metal substrate [24–54]. Also, our previous studies have revealed that conditions of the electrolyte solution such as pH and kind of dissolved ionic species have significant effects [43,44]. Regarding cathodic waves appeared in linear sweep voltammetry, Aoki and Kakiuchi have developed a method to simulate them with consideration of the above-mentioned van der Waals forces between neighboring alkanethiol molecules. The computational drawing expresses well the characteristic cathodic wave of the voltammogram, which is negatively shifted and narrowed with an increase in alkyl chain length of the SAM [55]. Furthermore, Kakiuchi has reported the modified way with consideration of fine structure of the SAM that can be improved by its annealing [56].

Although extensive studies have been made concerning ionic liquid as an electrolyte and electrochemical desorption of *n*-alkanethiol SAM, combination of both materials has not been studied, so far. Then, we have attempted it, focusing on roles of cations and anions in the desorption reaction. As shown in this paper, we found that the SAM was certainly desorbed by electrochemical reduction even in ionic liquid but that the desorption features were different from those observed in an aqueous electrolyte solution. In order to know factors causing such the differences, the experimentally obtained voltammograms with numerically simulated voltammogram curves. As mentioned above, Aoki and Kakiuchi groups have established two ways to simulate voltammograms with consideration of van der Waals interaction between alkyl chains of the SAM [55,56]. In this study, we adopted the first way developed by using the honeycomb model, in which a parameter (u_R) representing interaction between alkyl chain of the SAM as well as that (u_V) representing interaction between adsorbed thiol molecules and electrolyte solution are considered.

2. Experimental

2.1. Chemicals

The hydrophobic ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMI-TFSI), were synthesized by mixing aqueous solutions containing corresponding cation (EMI-Br or BMI-Br, Solvent Innovation Co., Ltd) and anion (Li-TFSI, Kishida Kagaku Co., Ltd.) species so as to give equivalent molar amounts of each species [7,20,57,58]. After vigorous mixing, the solution was spontaneously sep-

arated into two layers and the resulting ionic liquid isolated as a lower layer was washed with dichloromethane. The hydrophilic ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄), were purchased from Solvent Innovation Co., Ltd. All ionic liquids were dried under vacuum at 105 °C for 3 h at least prior to use. Four kinds of alkanethiols, *n*-propanethiol, *n*-hexanethiol, *n*-octanethiol and *n*-decanethiol, purchased from Wako Pure Chemical Ind., were of reagent grade and used without further purification. Their alkyl chain lengths will be indicated in this paper by numbers of carbon atoms (*n* of C_{*n*}H_{2*n*+1}SH).

2.2. SAM preparation and electrochemical measurements

An Au/mica electrode substrate having a quasi (111) surface was prepared by vacuum evaporation of Au on a freshly cleaved natural mica sheet (Nilaco Co.) heated at 290 °C. The electrode coated with the SAM of *n*-alkanethiol was prepared by immersing the Au/mica substrate in 1 mmol dm⁻³ alkanethiol/ethanol solution for 3 h at room temperature.

The electrochemical cell used was a Pyrex glass tube (ϕ 1.5 cm × 9 cm), both ends of which were open. The SAM-coated electrode was placed at the bottom hole of the cell with a silicone rubber O-ring (apparent electrode area of 0.36 cm²), and the top hole was tightly fitted with a silicon rubber stopper having a Pt foil counter and Ag/Ag⁺ (0.1 M) reference electrodes [59–62]. The effective surface area of the electrode, which was determined from the electric charges of anodic oxidation of chemically adsorbed iodine [63], was 0.40 cm². Linear sweep voltammetry was conducted using a computer-controlled potentiostat (Hokuto Denko HSV-100) in a glovebox circulated with purified argon gas (inner temperature of 30 °C).

2.3. Numerical simulations of linear sweep voltammograms

Computational simulation of linear sweep voltammograms was carried out using a program that was composed by Visual Basic 6.0 based on a formula considering the stabilizing energies due to thiol–thiol and thiol–solvent interactions [24,45–55].

3. Results and discussion

3.1. Reductive desorption of *n*-alkanethiol SAM in KOH aqueous solution

Fig. 1 shows linear sweep voltammograms taken in 0.5 M KOH solution for Au(111) electrodes coated with *n*-alkanethiol SAM having different alkyl chain lengths. Each voltammogram shows a cathodic wave indicating reductive desorption of the alkanethiols, and its peak potential is negatively shifted and its width becomes narrow with an increase in chain length. When the alkyl chain

Download English Version:

<https://daneshyari.com/en/article/220725>

Download Persian Version:

<https://daneshyari.com/article/220725>

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