論文 / 著書情報
Article / Book Information

題目(和文)	室温イオン液体膜内に原子金装飾ポリアニリン/プラチナ複合材 料を使用した小型電流測定ガスセンサー
Title(English)	Miniaturized amperometric gas sensor with atomic gold decorated polyaniline/platinum composites in room temperature ionic liquid film
著者(和文)	Anifatul Faricha
Author(English)	Anifatul Faricha
出典(和文)	学位:博士(学術), 学位授与機関:東京工業大学, 報告番号:甲第12590号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:中本 高道,小池 康晴,小尾 高史,長谷川 晶一,曽根 正人
Citation(English)	Degree:Doctor (Academic), Conferring organization: Tokyo Institute of Technology, Report number:甲第12590号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	Information and Communications Engineering 系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of (Philosophy)
学生氏名： Student's Name	Anifatul Faricha	審査員主査： Chief Examiner	Takamichi Nakamoto

要旨（和文2000字程度）
Thesis Summary（approx.2000 Japanese Characters）

In this doctoral work, we fabricated the atomic gold on a miniaturized amperometric gas sensor (AGS) coated with several room temperature ionic liquids (RTILs) with applying electrochemical (EC) potentials to achieve a high sensitivity of gaseous butanol isomers measurements. The sensor array was also checked to obtain a good capability of butanol isomers discrimination. The miniaturized AGS used an interdigitated array (IDA) electrode; the working electrodes (WEs), counter electrode (CE), and reference electrode (RE) were made of platinum and deposited onto a single glass substrate with dimensional size of 12 (width) x 20 (length) x 0.5 (thickness) mm, which is much smaller than AGS with liquid electrolyte.

Firstly, the possibility of using RTILs on IDA electrode (without atomic gold) was investigated. In this study, we also incorporated the gravimetric sensor, i.e., quartz crystal microbalance (QCM) coated with same RTILs applied in AGS to check the solubility of the analytes (e.g., 1-butanol, isobutanol, 2-butanol). QCM was selected due to a high stability and sensitive to mass change. We explored RTILs with different cation and anion combinations, i.e., 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium bromide, and 1-hexyl-3-methylimidazolium chloride identified as [EMIM][Ac], [BMIM][Br], and [HMIM][Cl], respectively. The cation was varied from high to low alkyl hydrocarbon chain with the order of $[HMIM]^+$ > $[BMIM]^+$ > $[EMIM]^+$. Although using a high cation chain has a slow mass transport, it has a high viscosity which is beneficial to keep its shape in a long period if a thin RTIL film is used as coating. From this perspective, we investigated different cations including a high alkyl hydrocarbon chain applied on miniaturized AGS. Three different anions were used, i.e., $[Ac]^-$, $[Br]^-$, $[Cl]^-$. A particular pair of cation and anion forming RTIL has a certain physical and chemical property like the electrochemical window (ECW) potentials more than 2 V. The [EMIM][Ac], [BMIM][Br], and [HMIM][Cl] have the ECWs of 3.2 V, 2.7 V, and 2.9 V, respectively. QCMs were coated with [EMIM][Ac], [BMIM][Br], and [HMIM][Cl] using dip-coating method. Based on the QCM results, butanol isomers were soluble in [EMIM][Ac], [BMIM][Br], and [HMIM][Cl] with obtained different frequency change magnitudes. Furthermore, for electrochemical sensor, since the IDA's RE was made of Pt, the Ag/AgCl ink was applied, painted, and dried for two days on Pt. Then, 5 µL of RTIL was coated on IDA where WEs, CE, and RE were covered. The six EC potentials for each RTIL were applied for butanol isomers measurements. According to the obtained results, [EMIM][Ac], [BMIM][Br], and [HMIM][Cl] can be used as the electrolyte in the miniaturized AGS. In addition, the IDA coated with [EMIM][Ac] with certain EC potential had the highest sensor response, contributed to a good selectivity, and achieved a linear concentration dependency. Therefore, in the second research stage, for modified IDA with atomic gold, RTIL having short alkyl hydrocarbon cation of $[EMIM]^+$ was selected. For the butanol isomers separation, the lowest Wilk's lambda, i.e., the pattern separation index, 4.82×10^{-8} was achieved by two sensor types combination, i.e., QCMs (coated with RTILs of [EMIM][Ac], [BMIM][Br], and [HMIM][Cl]) and IDAs (coated with [EMIM][Ac] at +0.25 V, +0.5 V, and +0.9 V).

To enhance the sensitivity of butanol isomers measurement, the atomic gold was doped at working electrode of IDA. In this stage, the selected RTILs were applied, i.e., [EMIM][Ac], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate

([EMIM][Otf]), and 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]). The different anions were used; $[Otf]^-$ and $[Cl]^-$ were chosen because their conductivities are higher and lower than $[Ac]^-$, respectively. The solubility of butanol isomers in selected RTILs were also checked using QCMs coated with the same RTILs. Based on the results from QCMs, the butanol isomers were soluble in [EMIM][Ac], [EMIM][Otf], and [EMIM][Cl] with the obtained frequency changes as their sensor response. For the atomic gold deposition, the polyaniline (PANI) was chosen as the host matrix. PANI was polymerized on IDA electrode in the Sone Laboratory, Tokyo Institute Technology, Japan. Afterwards, the deposition process of atomic gold (i.e., Au_2 clusters) on Pt/PANI and its verification was carried out in the Nakamoto Laboratory, Tokyo Institute Technology, Japan. The electro-oxidation obtained from cyclic voltammogram curve of propanol isomers in KOH was used to verify the success of Au_2 clusters formation decorating Pt/PANI. The Ag/AgCl ink was painted and dried for two days on IDA's reference electrode. Afterward, 5 µL of RTIL was coated on IDA where RE, CE, and WEs were covered. Based on the results, using [EMIM][Ac], [EMIM][Otf], and [EMIM][Cl] for all investigated fixed EC potentials, mostly, Pt/PANI/Au_2 had higher sensor response than Pt/PANI/Au_0 meaning that Pt/PANI/Au_2 enhanced the sensitivities to butanol isomers and atomic gold of Au_2 was catalytically active in these RTILs. In addition, the concentration dependency trends varied more linearly using Pt/PANI/Au_2 than Pt/PANI/Au_0. For the discrimination capability of butanol isomers, the lowest Wilk's lambda of 7.24×10^{-4} was obtained by combination of two sensor types, i.e., QCMs (coated with [EMIM][Ac], [EMIM][Otf], and [EMIM][Cl]) and IDAs (coated with [EMIM][Ac] at +0.5 V, [EMIM][Otf] at +0.5 V, and [EMIM][Cl] at +0.5 V).

For QCMs, although different sensing films were used, i.e., [EMIM][Ac], [BMIM][Br], [HMIM][Cl], [EMIM][Otf], and [EMIM][Cl], the results showed that the distance between 1-butanol group and isobutanol group were close compared to 2-butanol group. When combining with QCMs information with IDA, the discrimination capability of butanol isomers obtained using IDA with atomic gold (Pt/PANI/Au_2) was not as good as using IDA without atomic gold (Pt only). It was because Pt/PANI/Au_2 enhanced the sensitivity of all analytes. Pt/PANI/Au_2 having higher sensor response to isobutanol than IDA without atomic gold.

The atomic gold decorating miniaturized AGS was catalytically active in RTILs which was successfully demonstrated and verified in this research. In addition, the combination of RTILs and EC potentials into an array contributed to the enhanced discrimination capability among butanol isomers.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note：Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

注意：論文要旨は、東工大リサーチリポジトリ(T2R2)にてインターネット公表されますので、公表可能な範囲の内容で作成してください。
Attention: Thesis Summary will be published on Tokyo Tech Research Repository Website (T2R2).