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Electrochemical reduction of CO_2 to ethylene glycol on imidazolium ion-terminated self-assembly monolayer-modified Au electrodes in an aqueous solution

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Imidazolium ion-terminated self-assembled monolayer (SAM)-modified electrodes achieve CO_2 conversion while suppressing hydrogen evolution. Immobile imidazolium ion on gold (Au) electrodes reduce CO_2 at low overpotential. The distance between electrode and imidazolium ion separated by alkane thiol affects CO_2 reduction activity. CO_2 reduction current depends on the tunnel current rate. Although the product of CO_2 reduction at the bare Au electrode is CO, SAM-modified electrodes produce ethylene glycol in aqueous electrolyte solution without CO evolution. The faradaic efficiency reached a maximum of 87%. CO_2 reduction at SAM-modified electrodes is unaffected by reduction activity of Au electrode. This phenomenon shows that the reaction field of CO_2 reduction is not the electrode surface but the imidazolium ion monolayer.

1. Introduction

To resolve energy issues caused by the depletion of fossil fuels, a variety of sustainable and renewable energy sources are required. One of the candidates is artificial photosynthesis. In artificial photosynthesis, despite numerous reports on water splitting to generate H_2 using solar energy or solar-derived electricity, photoelectrochemical reduction of carbon dioxide (CO_2) is difficult.[1] Because CO_2 is one of the most electrochemically stable molecules, conversion of CO_2 to fuels and useful organic chemicals constitutes a great challenge. By electrochemically reducing of CO_2 at metallic electrodes in an aqueous solution, carbon monoxide (CO) or formic acid is usually obtained, which can be further reduced to formaldehyde and to methanol and finally to methane. These reduction reactions are investigated despite the expense of large overpotential and low faradaic efficiency,[2] because CO_2 radical anion is produced in a first single-electron reduction step to activate CO_2 molecule for subsequent second-electron reduction. Copper is the only electrode material capable of producing highly reduced carbon compounds.[3] Although in nonaqeuos electrolyte, CO_2 can be converted to various products such as CO, formic acid, oxalate, glyoxylate, glycolate, tartante and malate without hydrogen evolution, reduction of CO_2 requires the application of very large negative potential.[4] The enhancement of CO_2 reduction in an aqueous or nonaqeuos solution by adding ionic liquids (imidazolium salts) has recently been investigated. Rosen reported selective conversion of CO_2 to CO at low overpotential on silver catalyst in an aqueous solution of ionic liquid electrolyte.[5] Ionic liquid on silver surface suppresses H_2 generation and enhances CO_2 conversion by forming a complex such as CO_2-ionic liquid. Bocarsly investigated CO_2 reduction at illuminated iron pyrite electrodes in an aqueous solution containing imidazolium salts.[6] The imidazolium is catalytic for the reduction of CO_2. It is speculated that N-heterocyclic carbene or ylide electronic structure is generated electrochemically at the C2 ring position of imidazolium. CO_2 interacting with the C2 ring position is reduced to formic acid. Electrochemical carboxylation at the C2 position of imidazolium-based ionic liquid is characterized by ^1H NMR spectrum of a precipitate generated in the reduction of CO_2.[7] Thus, to decrease overpotential and to select the various products of the reduction of CO_2, it is important to control the imidazolium-CO_2 intermediate on the electrode surface.

Chemical modification of the electrode surface is one way of controlling selectivity for reaction.[8] Monolayer-modified electrodes can be constructed with self-assembly techniques to form a well-ordered molecular layer.[9] Therefore, self-assembled monolayer-modified electrodes have been studied with a view to elucidating the relations between structure and electrochemical reactions.[10, 11, 15]

To reduce CO_2 without H_2 generation, it is necessary to make a low-free-energy complex of CO_2 preferentially on the electrodes. Therefore, we developed novel imidazolium ion-terminated self-assembly monolayer-modified Au electrodes. It is possible that immobile-imidazolium ion on gold (Au) electrodes accelerates the CO_2 reduction reaction and

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suppresses H_2 generation. Changing of the methylene unit lengths from thiol termination to imidazolium ion is expected to affect selectivity for electrochemical reduction of hydrogen ion and CO_2 molecule. Moreover, it is confirmed that the CO_2 reduction compounds are different at imidazolium ion-modified Au electrode and bare Au electrode, respectively. In this paper, we clarify the relations between selective CO_2 reduction and the roles of self-assembled monolayer (SAM) on Au electrodes.

2. Experimental section

2.1 Synthesis of thiol-terminated 1-methylimidazolium salts

For the preparation of chemically modified electrodes, thiol-terminated 1-methyl-imidazolium salts having different alkyl length (IL-2, IL-6, IL-8, and IL-12) were synthesized as follows: by reaction of 1-methylimidazole with dibromoalkane (methylene units = 2, 6, 8 and 12) followed by substitution with potassium thioacetate and then saponification with NaOH and acidification with HBr. Thus we obtained four thiol-terminated 1-methylimidazolium salts:[11]
IL-2: 1-(-2-mercaptoethyl)-3-methylimidazolium bromide,
IL-6: 1-(-6-mercaptohexyl)-3-methylimidazolium bromide,
IL-8: 1-(-8- mercaptooctyl)-3-methylimidazolium bromide,
IL-12: 1-(-12-mercaptododecyl)-3-methylimidazolium bromide.

2.2 Preparation of chemically modified electrodes

The electrochemical cleaning by cyclic voltammetry (CV) was performed in a one-compartment electrochemistry cell with gold working electrodes, an Ag / AgCl reference electrode (3.0 M NaCl, RE-1B, BAS), and Pt spiral wire as a counter electrode.[12] All electrochemical measurement was carried out using a potentiostat / galvanostat (Solartron Analytical 1470E). Cleaned Au working electrodes (Au-coated silicon wafer, Sigma-Aldrich) were treated by electrochemical cycling between -300 mV and +1500 mV for Ag / AgCl in 1 M H_2SO_4 prepared by sulfuric acid (Kanto Chemical) at a scan rate of 150 mVs^{-1} for 1 hour and then 50 mVs^{-1} for 10 min. Reproducible cyclic voltammogram was obtained by electrochemical cleaning. (Supporting Information, Figure S1) X-ray diffraction (XRD) patterns and Atomic Force Microscope (AFM) images were collected to investigate the morphology and composition of the cleaned gold surface. (Supporting Information, Figure S2 - S3) To form SAMs on gold electrodes, 10 mM ethanolic solutions of thiol-terminated 1-methyl-imidazolium salts (IL-2, IL-6, IL-8, and IL-12) were prepared, respectively. The Au electrodes were sunk into the respective solutions in an airtight container for at least 24 h at room temperature. The chemically modified Au electrodes were rinsed with both ethanol (Kanto Chemical) and distilled water and then dried with nitrogen (N_2) gas stream. Figure 1 shows a schematic of SAM-modified Au electrodes. Electrochemical cleaning by CV without SAM modification was applied to bare Au electrode. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the samples were obtained for the investigation of a SAM-modified Au electrode surface (Supporting Information, Figure S4).

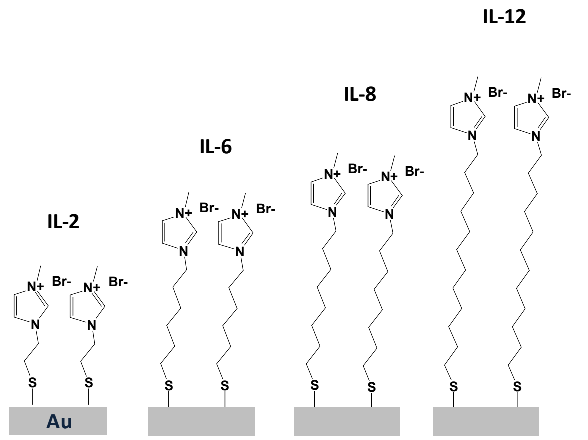


Figure 1. Schematic of Au electrodes with 1-methylimidazolium-terminated SAMs (IL-2, IL-6, IL-8, and IL-12).

2.3 Electrochemical measurements

The electrochemical measurement of cyclic voltammetry (CV) was performed in the one-compartment electrochemistry cell with gold working electrodes (1.5 cm^2), an Ag / AgCl reference electrode (3.0 M NaCl, RE-1B, BAS), and Pt spiral wire as a counter electrode. The electrolyte solutions were 0.5 M Na_2SO_4 aqueous solution or 0.5 M $NaHCO_3$ aqueous solution prepared by using sodium sulfate and sodium hydrogen carbonate (Wako Pure Chemicals), respectively. The electrolyte for the H_2 evolution experiment was Na_2SO_4 aqueous solution prepared by bubbling N_2 gas. For CO_2 reduction experiments, Na_2SO_4 or $NaHCO_3$ saturated with CO_2 was used. CO_2 or N_2 gas was bubbled into the solution for at least one hour before the measurements. For all cyclic voltammetry measurements, potential sweep was repeated until a reproducible voltammogram was obtained. All potential values were measured against an Ag / AgCl reference electrode and converted to the RHE (Reversible Hydrogen Electrode) scale using $E (\text{vs. RHE}) = E (\text{vs. Ag / AgCl}) + 0.0591 \text{ V} \times \text{pH} + 0.195 \text{ V}$.

For detection and qualitative analysis of the electrolysis product, a steady-state bulk electrolysis experiment was carried out in 0.5M $NaHCO_3$ aqueous solution saturated with CO_2. Electrolysis was performed in a gas-tight two-compartment electrochemical cell with proton exchange membrane (Nafion117, Du Pont) as a separator. (Supporting Information, Figure S5) Each compartment contained 10.0 mL electrolyte. Gold working electrodes (bare or modified IL-2) were held at -0.58 V for RHE. The electrolyte in the cathodic compartment was stirred at a rate of 800 rpm during electrolysis. CO_2 gas was delivered into the cathodic compartment at a rate of 50.0 sccm. The gas-phase products were detected using a gas chromatograph (Agilent GC System 7890A; Column: GS-GASPRO 30 m × 0.320 mm). An analytical sample was extracted from the cathodic compartment every 15 mines. The liquid-phase products were analyzed by an ion chromatograph (Waters IC System; 2695 Separation Module equipped with Waters 432 Conductivity Detector; Column: Thermo Dionex™ IonPac™ AS11 4 mm × 250 mm and AG11 4 mm × 50 mm) and gas chromatograph (Agilent Technologies HP 6890; Column: DB-WAX 0.25 mm × 30 m × 0.25 µm). An analytical sample was extracted from the cathodic compartment every hour. The Faradaic efficiency was monitored from the charges flowed during the reduction period.[13]

3. Results and discussion

Figure 2 shows CV curves of the bare Au electrode and SAM-modified Au electrodes in N_2- or CO_2-purged 0.5 M Na_2SO_4 aqueous solution. Because the pH of CO_2-purged Na_2SO_4 aqueous solution was changed from 5.6 to 4.3, the pH of N_2-purged Na_2SO_4 aqueous solution was adjusted to 4.3 by adding H_2SO_4.[14]

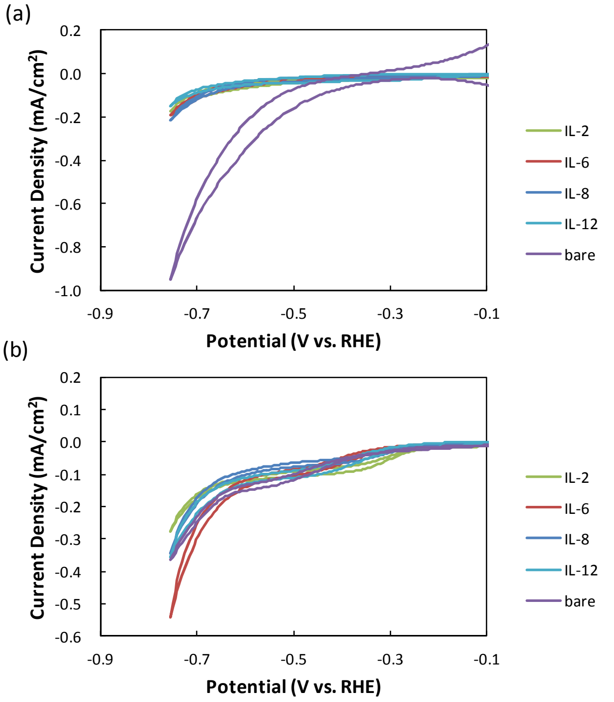


Figure 2. Cyclic voltammogram of the Au and SAM-modified Au electrodes in Na_2SO_4 aqueous solution purged with (a) N_2 and (b) CO_2. Scan rate: 100 mVs^{-1}.

Reduction current in the N_2-purged Na_2SO_4 aqueous solution was flowed by hydrogen evolution reaction (HER) for both bare and SAM-modified Au electrodes (Figure 2(a)). However, HER current at the bare Au electrode was larger than at the SAM-modified Au electrodes and started to flow at a more positive potential (around -0.3 V for RHE), and HER current was the same for every SAM-modified Au electrode. HER active site was only the underlying Au electrodes at both bare and SAM-modified electrodes. Lee reported an investigation of the selective reactivity of IL-based SAM-modified Au electrodes in which $Ru(NH_3)_6Cl_3$ was used as a cationic redox probe molecule.[15] The SAM containing imidazolium ion acted as insulating layers for the positively charged redox molecule, $Ru(NH_3)_6^{3+}$, by electrostatic repulsion force (Supporting Information, Figure S6). The SAM containing imidazolium salts at Au electrodes increased HER overpotential by preventing the closing of hydrogen ion (positively charged ion). Therefore, HER activity of the SAM-modified Au electrodes was low and small reduction current was obtained at all Au electrodes with SAM. It is speculated that the failure to completely prevent HER is attributable to the presence of a few defects or the lack of a closely packed structure in the SAM on Au electrodes (Supporting Information, Figure S4).

In the CO_2-purged Na_2SO_4 aqueous solution, reduction current was flowed by HER and CO_2 reduction reaction (Figure 2(b)). An Au electrode is known to be highly active for CO_2 reduction to CO.[2] However, Sun reported that Au catalyst with organic molecular layer enhanced the CO_2 reduction reaction and that HER activity in the Na_2SO_4 aqueous solution was low.[14] Reduction current started to flow around -0.25 V with RHE at every Au electrode and mainly occurred as a result of the CO_2 reduction reaction. In comparison with HER in the N_2-purged Na_2SO_4 aqueous solution, reduction current starting HER in the CO_2-purged Na_2SO_4 aqueous solution flowed at a more negative value than around -0.6 V for RHE at every Au electrode. Every Au electrode similarly achieved selective CO_2 conversion at positive potentials toward HER. However, since the Na_2SO_4 aqueous solution did not provide an adequate supply of reactants for CO_2 reduction,[16] CO_2 reduction activity between the bare and SAM-modified Au electrodes was unclear.

Figure 3 shows CV curves of the bare Au electrode and SAM-modified Au electrodes that were investigated in the CO_2-purged 0.5 M $NaHCO_3$ aqueous solution. Reduction current in the CO_2-purged $NaHCO_3$ aqueous solution was flowed by HER and the CO_2 reduction reaction. Since the SAM-modified Au electrodes had especially low HER activity in the N_2-purged Na_2SO_4 aqueous solution, reduction current was mainly caused by the CO_2 reduction reaction in the CO_2-purged $NaHCO_3$ aqueous solution. Comparison of the bare and SAM-modified Au electrodes reveals that a large reduction current was obtained by imidazolium salts having small methylene units (reduction current: IL-2 > IL-6 > IL-8 > bare > IL-12) and started to flow at the positive potential (around -0.25 V for RHE). If the underlying Au electrodes were the only active CO_2-reduction sites and imidazolium-terminated SAM also prevented the supply of CO_2 molecules to the underlying Au electrodes, higher activity would not be obtained for the SAM-modified Au electrodes than for the bare Au electrode. Hence, CO_2 reduction did not occur mainly at the underlying Au electrode in SAM-modified Au electrodes. If imidazolium terminations on Au electrodes were close to one another, CO_2 reduction activity would be distance-independent. Since methylene unit length between imidazolium terminations and Au electrode affected CO_2 reduction activity, imidazolium terminations kept position with every methylene unit length on Au electrodes. Therefore, the active sites for CO_2 conversion share imidazolium terminations. Thus, we considered that imidazolium ion in SAM-modified Au electrodes was catalytic in that it lowered the reaction barrier (overpotential) of the reduction of CO_2 via an intermediate such as imidazolium-carboxylate and helped to suppress hydrogen formation.[6, 7, 14]

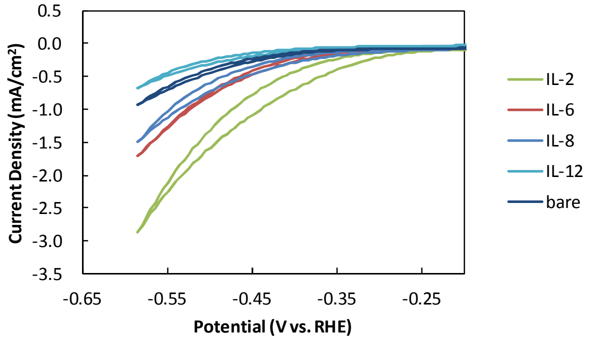


Figure 3. Cyclic voltammogram of the Au and SAM-modified Au electrodes in $NaHCO_3$ aqueous solution purged with CO_2. Scan rate: 100 mVs^{-1}.

The electron supply from an electrode to a molecule is necessary for the reaction with CO_2 at the molecule on the alkyl chain. In this case, the electron must move across an alkyl chain. One of the transport mechanisms across alkyl chains is the tunneling from an electrode to a molecule. If an alkyl chain is long, the tunneling rate is low. Therefore, the total reaction rate is limited by the tunneling rate in the case of long alkyl chain. The tunneling rate k_T is given by the following equation:

$$k_T = \frac{2\pi}{h} J^2 \delta(\varepsilon_E - \varepsilon_M) \quad (1),$$

$$J = \int \Phi_E^+ H \Phi_M dr \quad (2),$$

where J is a transfer integral between the Au electrode and the molecule on the alkyl chain, ε_E and ε_M are the electron energy at the electrode and the molecule, $\delta(x)$ is the delta function, h is the Planck constant, Φ_E and Φ_M are the wave function of the electrode state and the molecule state, and H is the total Hamiltonian (that depends on the insulating material). Integrating by r means integration of all space, and + means a Hermite conjugate. The delta function shows the conservation of electron energy. When the molecule level coincides with the electrode level by applying voltage, the electron can transport from the electrode to the molecule by tunneling.

It is well known that the tunnel distance (alkyl chain length) d dependence of the transfer integral can be evaluated as

$$J = J_0 \exp\left(-\frac{\beta}{2} d\right) \quad (3),$$

where J_0 is the constant (not dependent on d), and β is the decay constant of the transfer integral.[17] However, from eq. (2), the transfer integral depends on the state (the wave function) of the electrode (Φ_E) and the molecule (Φ_M). Therefore, β varies depending on a molecule. If the applied voltage is suitable for the tunneling, we can rewrite eq. (1) as,

$$k_T = k_0 \exp(-\beta d) \quad (4),$$

where k_0 in the case of is constant.

Figure 4 shows variations in reduction currents of CV at -0.58 V for RHE with the length of the alkanethiol between imidazolium termination and Au electrodes. Because the reduction current is proportional to the total reaction rate, the alkyl chain length dependence of Figure 5 is equivalent to the dependence of the reaction rate. This experimental result is in good accordance with eq. (4). The value of β is 0.14 per methylene. The value of β does not conform to the previously reported result for a different molecule, because the value of β depends on the molecule.[18] However, the value is within the range of the previously reported value. Thus, it is concluded that this rate is in good agreement with the tunneling model. Therefore, it became clear that CO_2 reacted with the molecule on the alkyl chain.

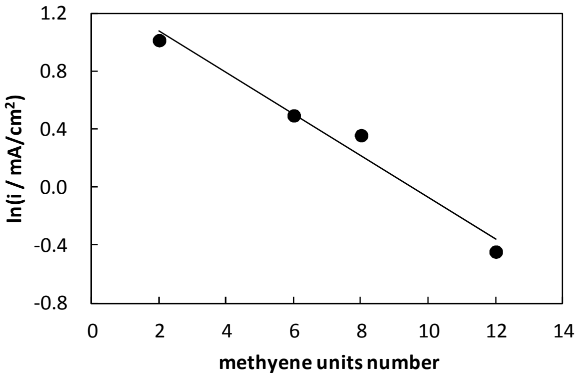


Figure 4. Variations in reduction currents of CV at -0.58 V vs. RHE in $NaHCO_3$ aqueous solution purged with CO_2 with the length of the alkanethiol between imidazolium termination and Au electrodes.

The CO_2 reduction activity was affected by distance dependence of electron transfer by the tunneling through the length of methylene units between imidazolium ion and Au electrodes. ILs-based SAMs were not the insulating layers for the positively charged redox molecule but electrocatalyst for CO_2 reduction reaction. As the number of methylene units in the alkyl chain on the SAM-modified Au electrodes decreased, the resistance to electron transfer through the SAM decreased and the electrocatalytic current for CO_2 reduction increased.

For detection and qualitative analysis of the electrolysis product, a steady-state bulk electrolysis experiment was carried out on bare and IL-2-modified Au electrodes at -0.58 V for RHE in the CO_2-purged 0.5 M $NaHCO_3$ aqueous solution. Figure 6 shows reduction currents, the faradaic efficiency and product amounts vs. time on bare and IL-2-modified Au electrodes. The product of CO_2 reduction at bare Au electrode was CO with the faradaic efficiency of 26% (Figure 6(a)). H_2 evolution of the faradaic efficiency (70%) approximately agreed with the value estimated from the remainder of the reduction current of CO formation.

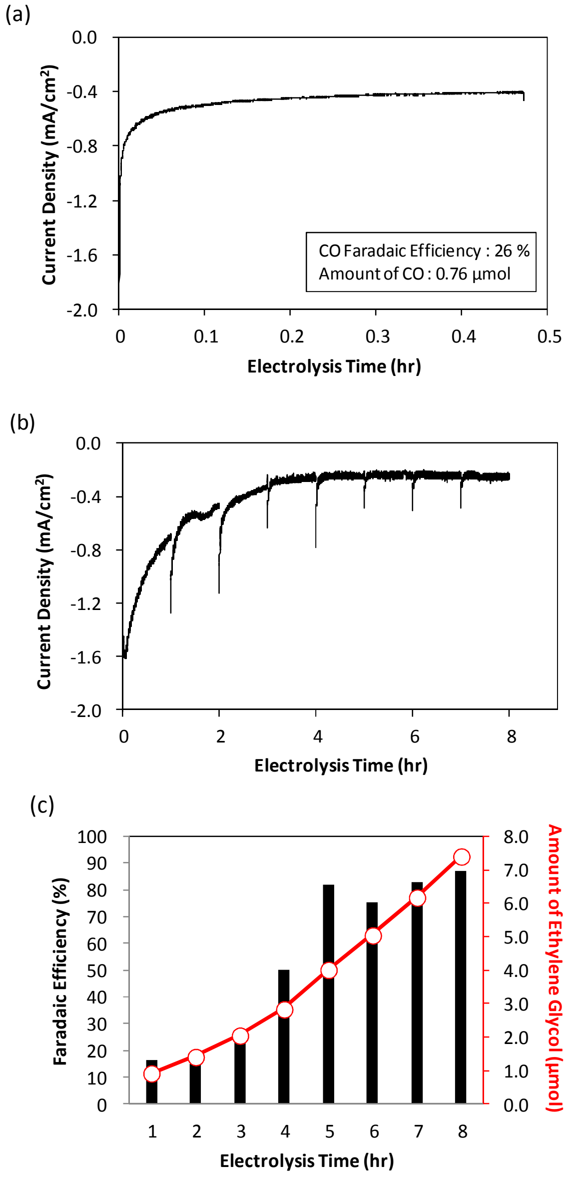
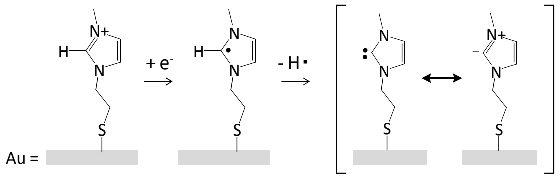


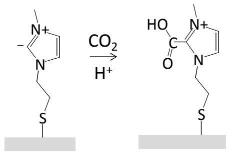
Figure 5. Reduction currents, the faradaic efficiency and product amounts vs. time on (a) bare and (b,c) IL-2 modified Au electrodes at -0.58 V vs. RHE in NaHCO$_3$ aqueous solution purged with CO$_2$. The Faradaic efficiency was monitored from the charges flowed during the reduction period ((a) for 15 min. (0.22 - 0.47 hours), (b,c) every hour).

In the case of electrochemical reduction of CO$_2$ at Au electrodes in aqueous solution, CO is usually obtained.[2] The product of CO$_2$ reduction at SAM-modified Au electrode was ethylene glycol (Figure 6(b,c), Supporting Information, Figure S7, 8). The faradaic efficiency of ethylene glycol increased with time and a maximum of 87% until equilibrium values were reached after 5 hours, and H$_2$ evolution of the faradaic efficiency accounted for the remainder of the CO$_2$ reduction current (Supporting Information, Figure S9). The amount of ethylene glycol continuously increased for 8 hours in electrolysis. It was confirmed that the SAM on Au electrodes has high selectivity of products and durability for aqueous solution, constant reduction potential and potential cycles (open ~ -0.58 V vs. RHE, every hour). If the SAM on Au electrodes had large defects, CO$_2$ would be reduced to CO by the supply of CO$_2$ molecules to the underlying Au electrode. However, ethylene glycol and H$_2$ were generated as products of reduction at SAM-modified electrodes without CO evolution (Supporting Information, Figure S10). If the SAM-modified electrodes have few defects, CO$_2$ reduction with SAM is highly active and unaffected by reduction activity of Au electrode. However, lead (Pb) electrode was known to generate oxalate or further reduced production in an aqueous or nonaqeuos electrolyte, CO$_2$ reduction was needed for high cathode potential (approximately 2 ~ 3V vs. Ag / AgCl), low selectivity and no ethylene glycol.[4] The imidazolium-terminated SAM on Au electrode reduces CO$_2$ at low overpotential by comparison of metal electrode such as Pb. Thus, CO$_2$ reduction at SAM-modified electrodes was essentially different from Rosen's reported mechanism and was considered to proceed as follows.[5] Imidazolium in SAM-modified Au electrodes was an immobile active site for CO$_2$ conversion by means of electron tunneling transport. In light of several reports,[6,7] N-heterocyclic carbene or ylide electronic structure was thought to be electrochemically generated at the C2 ring position of deprotonated imidazolium on Au electrodes at first, 5a;



(5a)

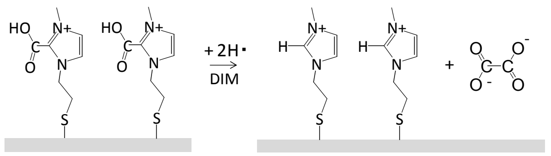
N-heterocyclic carbene or ylide electronic structure was a highly reactive species for water and oxygen. However, the electronic structure generally could not be kept in an aqueous electrolyte solution, and it was anticipated that Au electrode surface would bind imidazolium rigidly and stabilize the electronic structure to which a potential was applied continuously. CO$_2$ interacted with the C2 ring position of deprotonated imidazolium and a carboxylate species was produced, 5b;



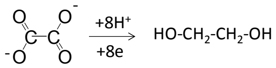
(5b)

Since the imidazolium of SAM on Au electrodes were close to one another, imidazolium carboxylate species were also positioned near one another. The only product of CO$_2$ reduction at SAM-modified Au electrode was ethylene glycol. C-C bond composed of ethylene glycol was necessary to couple two molecule of CO$_2$.

Imidazolium carboxylate species formed a dimer and this was followed by generation of oxalate and further reduction to ethylene glycol on the imidazolium catalysts of SAM, 5c-5d;

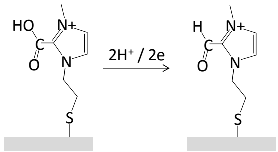


(5c)



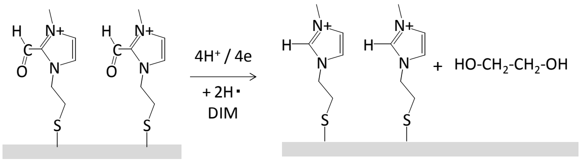
(5d)

In order to verify the reaction of 5c-5d, the electrolysis was carried out on IL-2-modified Au electrodes at -0.58 V vs. RHE in the electrolyte solution of 0.1 M oxalate dissolved in 0.5 M KCl. Ethylene glycol was not detected in the electrolyte solution after several hours of electrolysis. However, ethylene glycol was obtained in the electrolyte solution of 0.1 M glyoxal dissolved in 0.5 M KCl and the amount of ethylene glycol was increased with increasing electrolysis time. Thus, it is speculated that the reaction mechanism after 5b proceeds as follows: imidazolium carboxylate species was further reduced to imidazolium aldehyde species, 5e;



(5e)

Iimidazolium aldehyde species was followed by formation of a dimer and further reduction to ethylene glycol on the imidazolium catalysts of SAM, 5f;



(5f)

The faradaic efficiency of CO_2 reduction to ethylene glycol on SAM-modified Au electrode was highly selective (over 80%) without intermediate reduced products (oxalate, glyoxylate, glycolate, glyoxal and glycolaldehyde) or other C2 chemical compounds (acetic acid and ethanol). Thus, it was supposed that the intermediate, such as imidazolium-carboxylate, was stable for the CO_2 reduction reaction and accelerated conversion from CO_2 to ethylene glycol.

4. Conclusions

In summary, we have demonstrated that modification of the Au electrodes with novel thiol-terminated imidazolium salts accelerates CO_2 conversion while suppressing hydrogen evolution. CO_2 reduction activity was affected by distance dependence on the length of methylene unit between imidazolium ion and Au electrodes. Although the product of CO_2 reduction at bare Au electrode was CO, it was confirmed that ethylene glycol was generated as a product of CO_2 reduction at SAM-modified electrodes without CO evolution. As a result, we conclude that the active site for CO_2 conversion was imidazolium termination on SAM-modified Au electrodes. It is possible to construct the optimum reaction field for CO_2 conversion by using chemically modified electrodes with SAM.

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