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Online Electrochemical Mass Spectrometry Combined with the Rotating Disk Electrode Method for Direct Observations of Potential-Dependent Molecular Behaviors in the Electrode Surface Vicinity

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We newly developed a rotating disk electrode-online electrochemical mass spectrometry (RDE-OLEMS) to investigate potential-dependent molecular behaviors in electrode surface vicinity under mass transport-controlled conditions of reacting molecules. The potential-dependent molecular behaviors were investigated by using a quadrupole mass spectrometer (Q-mass) where the molecules are collected through a gas-sampling tip located in near the electrode surface. For the oxygen reduction reaction (ORR) on the polycrystalline Pt electrode, the potential-dependent Q-mass ion signal intensities of O_2 ($m/z = 32$) that are ascribable to the dissolved oxygen molecules increased linearly with the disk electrode rotation rates without substantial interference from the collection tip, clearly showing that the dissolved O_2 for ORR can be monitored by the RDE-OLEMS. For electrochemical carbon dioxide reduction (ECR) on the polycrystalline Au electrode, the potential-dependent Q-mass ion signal intensities of CO ($m/z = 28$) generated by the ECR increased with increasing disk rotation rates from 0 (without disk rotation) to 300 rpm in the potential region from -0.4 to -1.4 V vs. the reversible hydrogen electrode. The results demonstrate that the RDE-OLEMS enables us to evaluate the potential-dependent behaviors of reactant and product molecules present near the electrode surface under the mass transport-controlled condition.

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Electrocatalysis plays crucial roles in various electrochemical energy conversion systems, such as fuel cells,^{1–3} electrochemical carbon dioxide reduction,^{4,5} metal-air batteries,^{6,7} and water electrolysis.^{8–10} The total energy conversion efficiencies of the systems are limited mainly by the slow kinetics of either cathode or anode reactions. For example, because the cathode reaction rate, i.e., oxygen reduction reaction (ORR), for the polymer electrolyte fuel cells (PEFCs) is much slower than the hydrogen oxidation reaction (HOR) at the anode, a considerable amount of Pt is used for the cathode catalyst.¹¹ As for the electrochemical carbon dioxide reaction (ECR)¹² in aqueous solutions, although Au is a highly selective electrocatalyst for generating carbon monoxide (CO), the activity of the ECR for CO is low enough for wide spread use of practical ECR systems. Therefore, basic research on electrocatalysis and development of novel catalysts are performed widely aiming for highly-active, low-precious-metal-usage catalysts, by alloying,^{13–16} formation of core-shell nanostructures,^{17–20} etc.

Considering electrocatalysis that proceeds at the three-phase interface of solid-liquid-gas, not only the catalytic properties, e.g., activity, selectivity of catalyst surface, but also the mass transports of reacting molecules at the electrolyte-electrode interface determine the total efficiencies of the energy conversion systems.^{21–23} For example, Inaba et al. introduced gas diffusion electrodes (GDE) for benchmarking the performance of ORR catalysts. They showed that the ORR performance of the carbon-supported Pt catalysts is determined by the mass transport conditions of reacting oxygen molecules.²⁴ Furthermore, under the practical conditions of the ECR on the Au electrode, the electrode surface would be partly covered by the micro-bubbles of the CO and H_2 that is generated by the ECR and simultaneous hydrogen evolution reaction (HER), respectively. Therefore, the electrochemical surface areas (ECSA) and concentration of reacting molecules accessible to the electrode surface decrease under the practical condition, and thereby the fore-mentioned competing

electrochemical reactions (CO and H_2 generations) cannot be determined independently. To clear such hurdles for investigating the electrocatalysis, product molecules present near the electrode surface should promptly be removed, accompanied by a sufficient supply of the reacting molecules. Indeed, recent studies for the ECR using a gas diffusion electrode and electrochemical flow cell reactor revealed configurations of the electrochemical cells and how the CO_2 -supply seriously influences the total ECR efficiencies.^{25–28} Therefore, electrocatalysis studies conducted under various mass transfer-controlled conditions of reacting molecules should be of the utmost importance.

Differential electrochemical mass spectrometry (DEMS), or online electrochemical mass spectrometry (OLEMS) has been established^{29–34} and widely used for various electrochemical reactions to investigate the potential-dependent behaviors of reacting and product molecules. Recently, by using the DEMS system combined with the dual-thin layer flow cell, Chen et al. discussed the competition between ORR and HER on a polycrystalline Pt electrode in an acidic electrolyte under a constant forced convection flow.³⁵ The rotation disk electrode (RDE) technique can control the electrolyte convection flow^{36,37} to the working electrode surface and, thus, can be applicable to discuss various electrocatalysis under the mass-transfer conditions. However, no DEMS or OLEMS studies combining the RDE has been published yet for the reacting and product molecule behaviors of electrocatalysis under the mass-transfer conditions.

Therefore, in this study, we newly developed RDE-OLEMS to investigate potential-dependent molecular behaviors for both reactant and product molecules under the mass-transport-controlled conditions. The developed RDE-OLEMS, i.e., the homemade OLEMS setup^{38–40} combined with a conventional RDE apparatus, was applied for the reactant molecule of O_2 for ORR on the Pt electrode and the product molecule of CO by ECR on the Au electrode. The results obtained by the RDE-OLEMS clearly demonstrate that electrode potential-dependent molecular behaviors can be monitored not only for reactant molecules but also for product molecules under the mass transport-controlled conditions and that

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the RDE-OLEMS is a novel, quite powerful tool for investigating electrocatalysis.

Experimental

Figures 1a and 1b show a schematic view and a photograph of the RDE-OLEMS apparatus developed in this study, where the our homemade OLEMS setup^{38–40} that previously constructed by referring the pioneering work by Wonders et al.³¹ is combined with a conventional RDE apparatus. As shown in Fig. 1c, reactant (dissolved O_2 for ORR) and product molecules (H_2 for HER and CO for ECR) present near the electrode surface can be collected through a polyether-ether-ketone (PEEK)-made gas sampling tip, in which several pieces of porous Teflon (pore size = $10\ \mu m$) cut from a sheet were inserted. The distance between the tip and working electrode surface was fixed at $\sim 50\ \mu m$ by using a micrometer and by a CCD digital camera inspection. Figure 1d presents a magnified snapshot of a typical RDE-OLEMS measurement (disk rotation rate of 300 rpm). As shown in the snapshot, the distance between the tip and working electrode surface remained constant even under the disk rotation of 300 rpm. The gaseous components (reactant and product molecules) are introduced to a quadrupole mass spectrometer (Q-mass) attached to the vacuum chamber whose base pressure is approximately 1×10^{-6} Pa.

A homemade three-electrode electrochemical cell was used for the RDE-OLEMS measurements. Pt-wire and a $Ag/AgCl/3M-KCl$ electrode were used as a counter and reference electrode, respectively. A working disk electrode of polycrystalline Pt ($\phi = 5\ mm$,

$t = 4\ mm$, 99.99%, Nilako) with $0.1\ M\ HClO_4$ (Ultrapure, Kanto Chemical) electrolyte and that of Au ($\phi = 5\ mm$, $t = 4\ mm$, 99.99%, Nilako) with $0.1\ M\ KHCO_3$ (Analysis grade, Merck) were used for the ORR and ECR measurements, respectively. All the electrode potentials noted in this study were converted to the reversible hydrogen electrode (RHE). The Pt and Au disks, polished by the emery papers (#800, #1200, and #2000) and alumina pastes ($1\ \mu m$, $0.3\ \mu m$, and $0.05\ \mu m$), were ultrasonic cleaned in acetone (99.5%, Fujifilm Wako Chemical) and ultrapure water (Milli-Q). After that, the Pt or Au disk electrodes were attached to a rotating disk electrode (E5TQ, Pine Instrument) and the surfaces were re-cleaned by applying oxidation-reduction cycles between $0.05\ V$ and $1.5\ V$ at $500\ mV\ s^{-1}$ in each electrolyte, until the stable cyclic voltammograms of Pt and Au were obtained.

The RDE-OLEMS measurements were conducted as follows. For the dissolved O_2 in the ORR, linear sweep voltammetry (LSV) was conducted in O_2 -saturated $0.1\ M\ HClO_4$ by a negative potential sweep from $1.05\ V$ to $0.05\ V$ at a sweep rate of $0.5\ mV\ s^{-1}$ with the Pt disk rotation rate of 1200 rpm. The mass spectrometric LSV (MS-LSV) for the dissolved O_2 and applied-potential-dependent Q-mass ion currents (MS-LSVs) of O_2 ($m/z = 32$) were recorded simultaneously for the LSVs. For the ECR of CO , LSVs were recorded by a negative sweep from $0.0\ V$ to $-1.4\ V$ in CO_2 -saturated $0.1\ M\ KHCO_3$ aqueous solution at a sweep rate of $1\ mV\ s^{-1}$ with the Au disk rotation rates from 0 (without disk rotation) to 300 rpm. Simultaneously, MS-LSVs for the ECR product of CO ($m/z = 28$) and the HER product of H_2 ($m/z = 2$) were collected by the Q-mass.

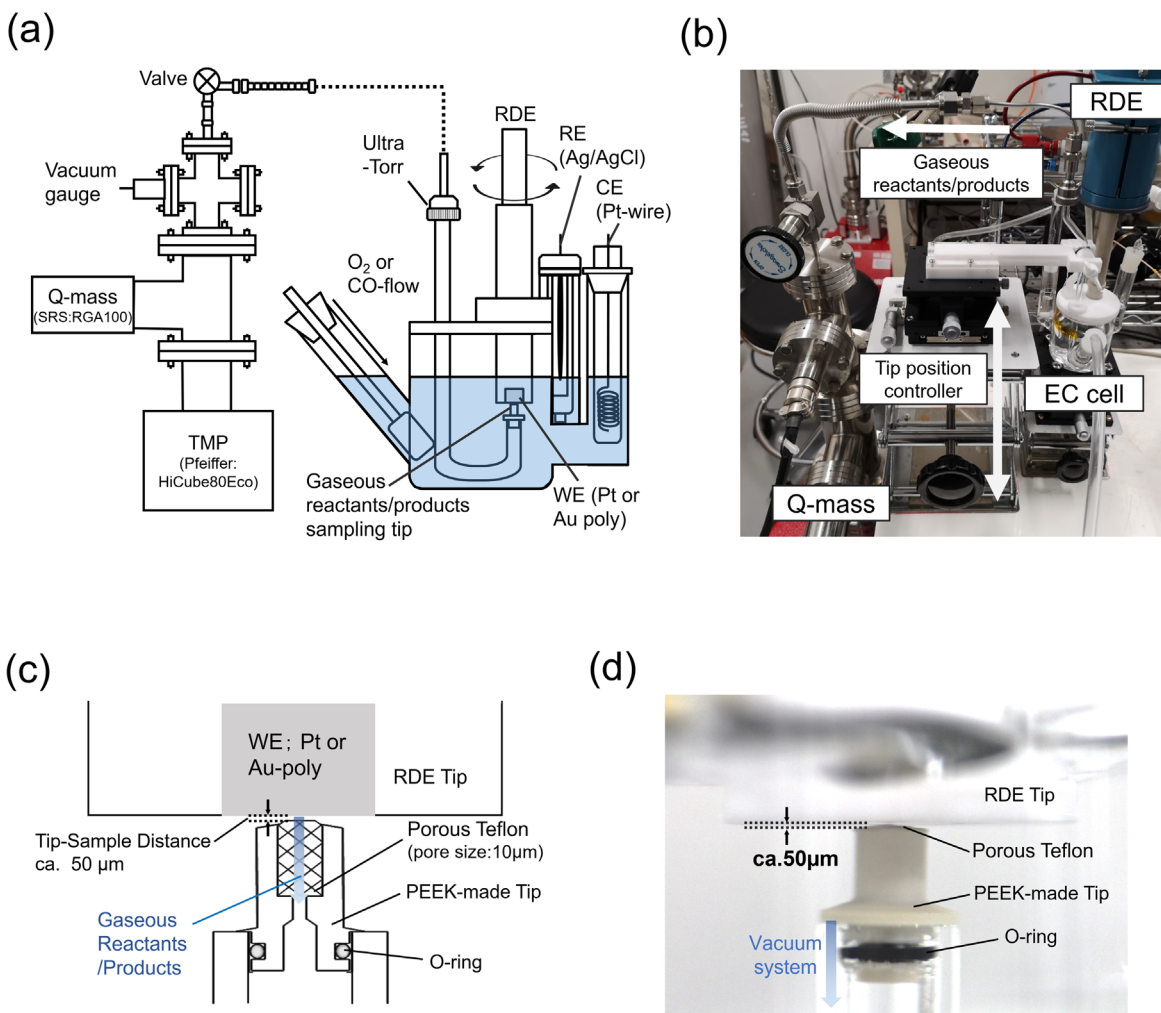


Figure 1. Schematic (a) and photograph (b) of RDE-OLEMS apparatus. Magnification schematic (c) and a snapshot (d) of the RDE-OLEMS measurement conducted under the disk rotation rate of 300 rpm.

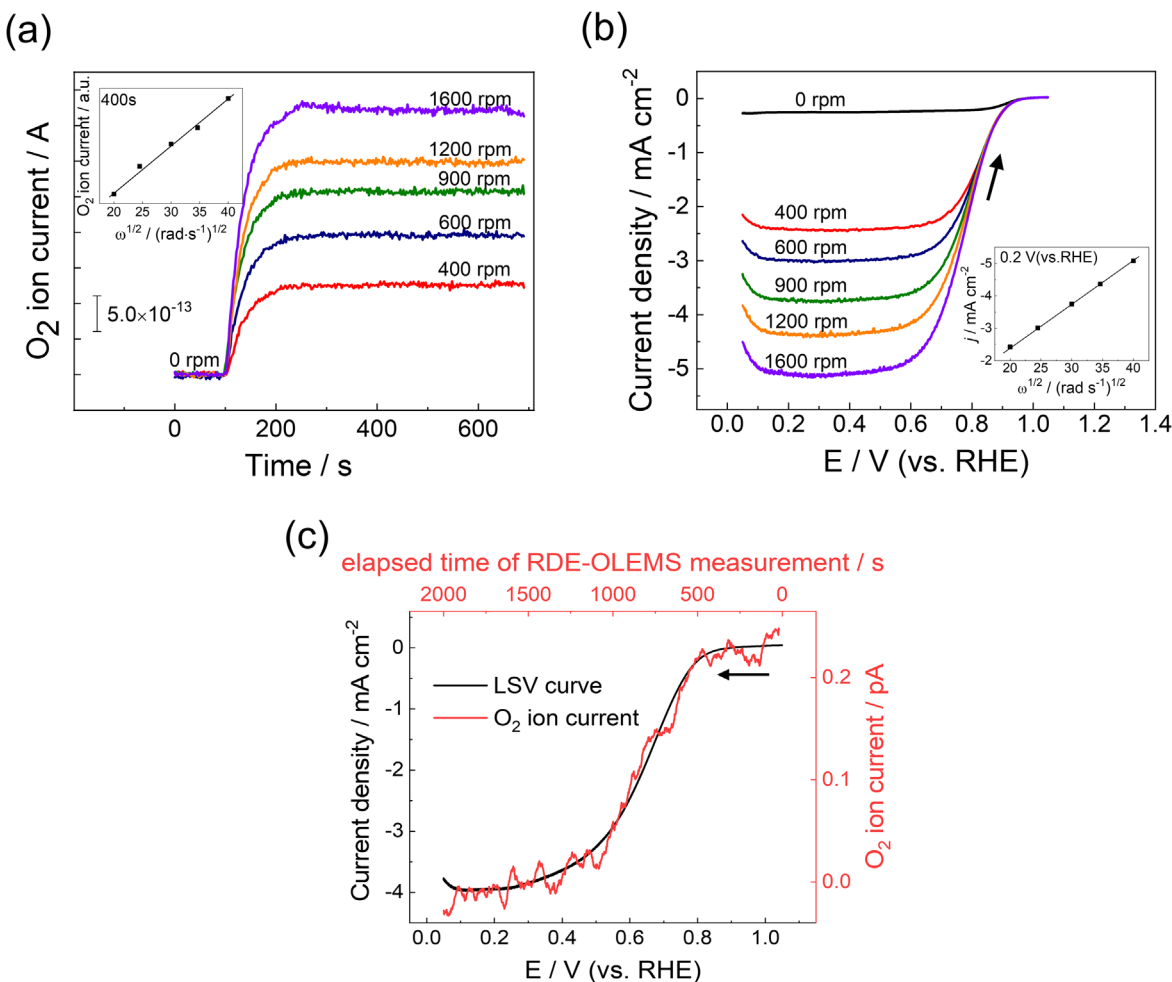


Figure 2. (a) Time-variations of O_2 ion currents ($m/z = 32$) measured by the Q-mass at a fixed potential of ~ 0.8 V (open circuit potential) for various disk rotation rates. Inset: The Q-mass O_2 ion currents at 400 s vs. square-root of the Pt disk rotation rates. (b) LSVs for ORR recorded in the positive-going potential sweep from 0.05 to 1.05 V with 10 mV s^{-1} . Inset: the Levich plot of ORR currents (j) at 0.2 V. (c) RDE-OLEMS measurements of the potential-dependent O_2 ion current (red; MS-LSV) and simultaneously recorded LSV curves (black) measured at 1200 rpm in the negative-going potential sweep from 1.05 to 0.05 V at a scan rate of 0.5 mV s^{-1} .

In this study, the measured MS-LSVs signals (Figs. 2a, 2b, 3b and 3c) are presented without any calibration.^{30,41}

Results and Discussion

Oxygen reduction reaction on Pt electrode.—Figure 2a shows the time-dependence of the Q-mass ion current intensities of O_2 ($m/z = 32$) at the fixed potential (open circuit potential ~ 0.8 V) measured as a function of the Pt disk rotation rates. The RDE-OLEMS measurements of the dissolved O_2 through the PEEK-made tip were started without disk rotation and, at 90 s, the rotations started for each rotation rate of 400–1600 rpm. The O_2 ion currents at stationary states (300–600 s) increased, depending on the disk rotation rates. We note that a retardation time of ~ 100 s was inevitable for a constant and stationary state detection of the target molecules dissolved in the electrolyte at the given disk rotation rates. In this set-up, the molecules present very surface vicinity of the working electrode were introduced into the Q-mass-equipped-vacuum-chamber through the several pieces of porous Teflon and the relatively narrow glass-made vacuum lines. Probably, the conductance is low against the pumping speed of the used turbo-molecular pump (671 min^{-1}), resulting in retardation of the Q-mass detection.⁴⁰ Figure 2b shows LSV curves of the Pt electrode surface recorded for a positive-potential sweep from 0.05 to 1.05 V at a scan rate of 10 mV s^{-1} by the RDE-OLEMS setup, where the PEEK-made tip is

located at $\sim 50 \mu\text{m}$ from the working disk electrode surface (Pt). The diffusion-limiting current regions for ORR from 0.2 to 0.6 V can be seen for all the LSVs. The insets in (a) and (b) depict the relation of the square root of the disk rotation rates with O_2 ion currents measured by the Q-mass (a) and ORR diffusion limiting currents ((b); Levich plot), respectively. Both the current values increased proportionally with the square-root of the disk rotation rates, indicating that the thicknesses of the diffusion layers can be controlled by the disk rotation rates even when the tip is located near the working electrode surface.

The MS-LSV and corresponding LSV measurements were conducted for ORR by a negative potential sweep (from 1.05 to 0.05 V); a scan rate of 0.5 mV s^{-1} with the Pt disk rotation of 1200 rpm. The MS-LSV (red) and LSV (black) are presented in Fig. 2c. The potential sweep direction, disk rotation rate, and potential scan rate were tuned considering the above-mentioned retardation times of the O_2 ion signal measured by the Q-mass.⁴⁰ As can be seen in (c), the Q-mass ion currents of O_2 (MS-LSV) correspond well with the ORR currents (LSV), demonstrating that the potential-dependent behaviors of the dissolved O_2 present near the electrode surface can certainly be monitored by the RDE-OLEMS.

Carbon dioxide reduction reaction on Au electrode.—Figure 3 summarizes LSVs for the ECR on the Au electrode (a) and the

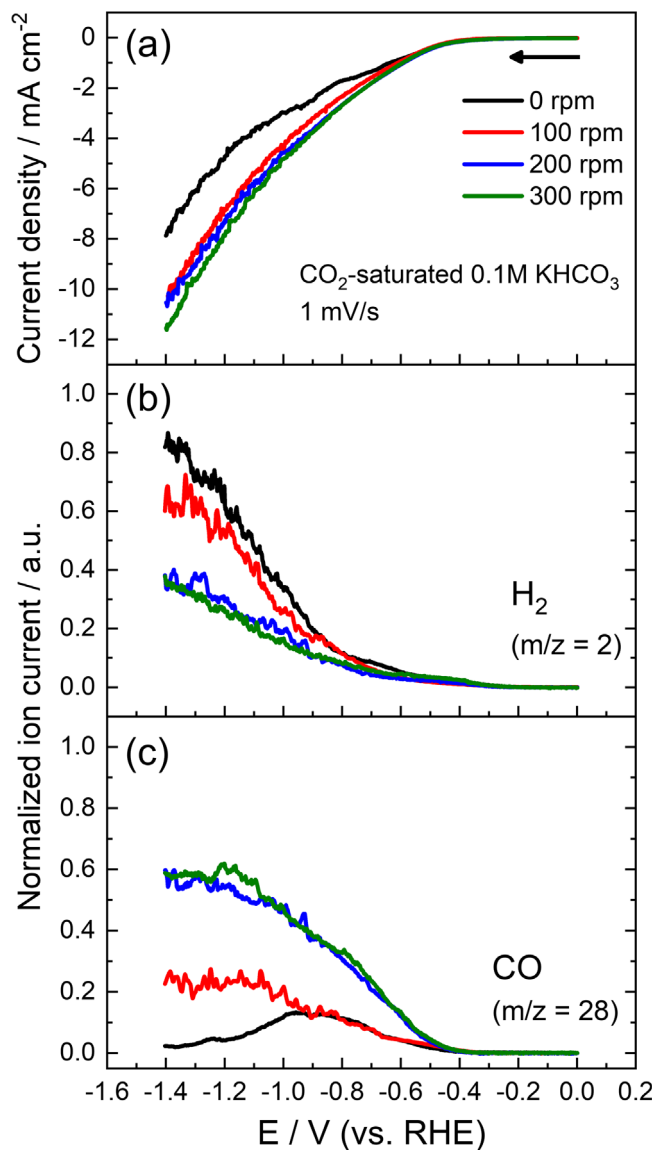


Figure 3. (a) LSVs of polycrystalline Au electrode recorded in CO₂-saturated 0.1 M KHCO₃ solution with sweep rate of 1 mV s⁻¹; the disk rotation rates were 0 (without rotation, black), 100 (red), 200 (blue), and 300 (green) rpm. Corresponding normalized ion currents (MS-LSVs) measured by the Q-mass for H₂ (m/z = 2) (b) and CO (m/z = 28) (c).

corresponding Q-mass-measured ion signals (MS-LSVs) for H₂ (m/z = 2) generated by HER (b) and ECR products of CO (m/z = 28) (c) with and without the disk rotations recorded with a sweep rate of 1 mV s⁻¹ in CO₂-saturated 0.1 M KHCO₃ aqueous solution. Irrespective of the disk rotation rates, the onset potentials of the LSVs (a) are approximately -0.6 V. In contrast, the current densities due to the ECR at lower potential regions than -0.6 V increased with increasing disk rotation rates from 100 to 300 rpm (a). As for the MS-LSV of H₂ (b), the onset potential is around -0.6 V and the Q-mass signals gradually decreased with increasing the disk rotation rates. The potential-dependent Q-mass signals recorded at disk rotation rates of 200 and 300 rpm were almost the same. On the other hand, the CO generation signals measured without the disk rotation (black in (c)) was much weaker than that for the H₂. Noticeably, the CO generation signals gradually increase with a negative-going potential sweep up to -1.0 V, then decrease with further potential sweep (below -1.0 V). In contrast, the

Q-mass-measured CO generations become active with increasing the disk rotation rates. For example, at 100 rpm (red), the Q-mass CO generation signals increase monotonically at the potentials below -1.0 V. Although the potential dependences for the 200 (blue) and 300 rpm (green) are similar to those for the 100 rpm, marked increases in signal intensities (almost triple vs 100 rpm) are obvious. The result indicates that mass-transport of the dissolved CO₂ to the Au electrode surface is accelerated by the disk rotation. Furthermore, the influence of the disk rotation becomes prominent at more negative applied potentials (relatively high current density region; below -1.0 V), probably because depletions of the dissolved CO₂ feeding to the ECR is compensated effectively by the disk rotation. We note that the recorded MS signal intensities should be determined not only by the mass transfer of the reactant CO₂, but also by the desorption rates of generated CO and H₂ molecules from the electrode surface. Complementary analysis by in situ techniques, like the electrochemical quartz crystal micro balances (EQCM), might be helpful for quantitative discussions of the different potential-dependent-molecular behaviors of CO and H₂.

As shown in Figs. 2 and 3, the MS-LSVs can be recorded successfully, demonstrating that the RDE-OLEMS is powerful for discussing electrocatalysis under the mass-transport-controlled conditions. However, relatively long retardation time (~100 s) is yet inevitable for detecting the dissolved O₂ molecules. Furthermore, by comparing the standard DEMS/OLEMS measurements,^{30,31} the slow sweep rate (0.5 mV s⁻¹) is necessary to obtain the well-fitted MS-LSV to electrochemical ORR currents (LSV). Thus, further refinements of the apparatus are required to establish the RDE-OLEMS method. Actually, in this study, the planar polycrystalline disks (Pt and Au) were used as the working electrodes for the ORR and ECR. As is obvious for the practical, high surface area catalysts with micro/macroporous structures, such as carbon supported metal (alloy) nanoparticles⁴² and nanoporous films,⁴³ the mass-transport phenomena of reactant molecules, such as O₂ and CO₂, as well as product molecules (CO, H₂, etc.), should be more crucial to discuss quantitatively the electrocatalytic efficiencies. Optimizations of the porous Teflon inserts, the glass tube, vacuum systems, Q-mass spectrometer etc., in the RDE-OLEMS set-up enable us to real time detection of the molecules present near electrode surface vicinity even for the practical catalysts. Such the refinements of the apparatus under the considerations of the effective diffusion and partition coefficients of the reactant and product molecules⁴⁴ should clarify the mass-transfer-effects on the ORR (reactant of O₂) and ECR (products of CO and H₂). Obviously, considering fore-mentioned features of the RDE-OLEMS, the system could be applicable for non-aqueous electrolytes,⁷ e.g., Li-O₂ battery,⁴⁵ by replacing the porous Teflon inserts to other suitable materials, by constructing the outer atmosphere-control electrochemical cells,⁴⁶ and by modifying the vacuum lines specialized for non-aqueous mediums.

Conclusions

In this study, we constructed a novel RDE-OLEMS apparatus to investigate the applied potential-dependence of reactant and product molecules under the mass transport-controlled conditions. The collection tip of the OLEMS does not substantially interfere with the convection flow of RDE and, thereby, the developed RDE-OLEMS enables the direct comparison of potential-dependent molecular behaviors based on the obtained MS-LSV and the simultaneously recorded LSV. As for ORR on the Pt electrode, the potential-dependent behaviors of the dissolved O₂ present near the electrode surface can be observed. Also, potential-dependent Q-mass ion currents due to the ECR to CO on the Au electrode were increased by the disk rotations, while that of H₂ generated by the competed HER decreased. The results indicate that the newly developed RDE-OLEMS is a powerful tool for investigating the dynamic behaviors of not only reactant but also product molecules of various electrocatalysis under the mass transport-controlled conditions.

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