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Author(s)	Minamimoto, Hiro; Osaka, Ryo; Murakoshi, Kei
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In-situ Observation of Isotopic Hydrogen Evolution Reactions using Electrochemical Mass Spectroscopy to Evaluate Surface Morphological Effect

Hiro Minamimoto*, Ryo Osaka, and Kei Murakoshi*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan.

Abstract

In the present article, the hydrogen evolution reaction in the mixed solution of H_2O and D_2O has been investigated on Pt and Ag electrodes via the electrochemical mass (EC-mass) spectroscopy. In addition to the metal species dependence, we have confirmed the morphological effect of the electrode surface on the isotopic effect. By the establishment of the EC-mass system, we have successfully discussed about the formation of the active sites which accelerated the hydrogen generation at the surface of Ag by the surface roughening process. The present results prove the importance of in-situ mass spectroscopic measurement for the investigation to establish the arbitrary control of the isotopic hydrogen evolution reactions.

1. Introduction

The hydrogen evolution reaction (HER) is one of the most investigated electrochemical reactions. HER is apparently simple electrochemical reaction. The actual reactions in HER, however, are quite complicated. During the HER process, three processes, i.e. adsorption, chemical recombination, and electrochemical recombination steps which are called as Volmer, Tafel, and Heyrovsky step, respectively, occur simultaneously at the electrode surface [1–4]. It is well known that the rate determining steps is quite sensitive to the metal species. Even though there are various reports on HER process at numerous electrode species, cooperative effect between elementary steps is still unclear. To consider the correlation between the reaction steps, the isotopic effect on HER could be useful for further improvement of the HER reactivity [5]. It has been revealed that the ratio of the generated H_2 and D_2, which are generally described as the separation factor (S_D), is sensitively influenced by the HER conditions, such as the mixed ratio of H_2O and D_2O, the solution temperature, over potential or the metal species [6–9]. According to the previous reports, the S_D value increases with increasing the over potential or the concentration of D_2O and saturates by exceeding the specific point while S_D value reduces by the temperature increase [9–11]. The arbitrary tuning of S_D is quite important not only for optimization of HER efficiency, but also development of the

techniques of the D_2O condensation or the efficient D_2 production in future.

To date, various both experimental and theoretical evaluations have been conducted for the clarification of the specific factor for the controlling the selectivity of the isotopic reaction. One of the useful method to tune S_D is to use the metal alloy, such as Fe or Ni alloy [12]. The principle of the tuning is based on the reaction characteristics that the isotopic reactivity strongly depends on the electronic state of the *d*-orbital of the metal species [13]. And also the dependence of the isotopic reactivity is described by the deference in the zero-point energy for H_2O and D_2O, resulting in the determination of the rate determining step as calculated previously [14]. The selectivity of the isotopic reaction is also affected not only by metal species, but also by additional factors, such as morphology, configuration of electrodes at the electrolysis, etc. However, especially in terms of high concentration of D_2O, the detail investigation of the isotopic effect with the concentration above 50% have never been examined because of the complex reaction process. The control of S_D would improve the efficiency of the industrial D_2O purification process. In order to specify the factors for the arbitrary control of S_D, it could be indispensable that the detailed monitoring of the isotopic reaction products in real time is correlated to the HER conditions.

The electrochemical mass spectroscopy which is the combination of the

electrochemical measurements with the mass analysis method realizes the *in-situ* observation of the reaction products originated from the faradaic current [15,16]. After the innovative establishment of the electrochemical mass spectroscopy in the beginning of 1970 s [17], various multiple electrochemical steps, such as the reduction of CO_2, the methanol oxidation, or H/D exchange reaction, have been investigated [18–21]. For example, the influences of methanol concentration or electrode structure on the current efficiencies of CO_2 production during methanol oxidation have been revealed as the function of the product selectivity [21]. The effect of the nitrate concentration and acidity on the reaction rate and selectivity of the electrochemical nitrate reduction on Pt electrode have been discussed via the quantitative analysis of the products [22]. Focusing on the ability of the electrochemical mass spectroscopy, it can be easily considered that the electrochemical mass spectroscopy would be the promising tool for the investigation of the isotope effect on HER process.

In the present article, we have reported the successful observation of *in-situ* electrochemical mass spectroscopic measurement on metal electrodes. By using our electrochemical mass spectroscopic system, we have found that novel isotopic selectivity of HER with relatively high concentration of D_2O on Ag electrodes with distinct morphology to compare with that of Pt. In present results, it is interesting that the curious

reaction selectivity tuning by the surface morphological was observed only in the case for Ag electrode. Through the *in-situ* analyses, mechanistic studies on the surface morphological effect on the isotopic reaction selectivity become possible. The present findings would provide important aspects for future methods to control the reaction selectivity of the isotopic HER.

2. Experiment

2.1. Electrochemical *in-situ* mass measurement system

The electrochemical HER has been conducted with a handmade three-electrode electrochemical cell. The working electrodes were Ag (99.99%) and Pt wires (99.98%) purchased from Tanaka Kikinzoku Kogyo, Corp. Ltd., Japan. The counter and reference electrodes were Pt plate and Ag/AgCl, respectively. Before the experiments, the working electrode was polished with the alumina particles. The supporting electrolyte was 0.5 M Na_2SO_4. For the isotopic HER, the deuterium (99.9% D_2O, Sigma-Aldrich, Japan) was used without any purifications. The mixed electrolyte solution was prepared by the mixing of H_2O (0.991 g, 0.99 mol) and D_2O (9.91 g, 9.01 mol), leading to 90wt% D_2O.

The reaction productions were analyzed by a quadrupole mass spectrometer, Q-mass (Qulee-HGM, 202, ULVAC Co., Japan) attached to the handmade electrochemical

cell. The generated gases are immediately flowed to the mass spectrometer through the capillary. For avoiding the insertion of the solution into the system, the capillary was coated with the porous Teflon membrane with the pore size of 10 μm. The pressure in the mass spectrometer chamber was set to less than 1.0×10^{-5} Pa. The schematic illustration of the *in-situ* mass analysis system was given in Fig. 1. All measurements have been performed under ambient temperature.

2.2. Surface roughening of Ag and Pt electrode

The surface roughening of Ag and Pt was conducted by following the well-established electrochemical oxidation reduction cycles. The Ag electrode was immersed into 0.5 M KCl aqueous solution. Then, the electrode potential of Ag was scanned from −0.3 to 0.3 V with the scan rate of 10 mV / sec for three cycles [23]. For the Pt case, the electrode potential of Pt was oscillated between −0.3 and 1.7 V with the frequency of 2 kHz in 0.5 M H_2SO_4 aqueous solution [24]. Through these processes, we have obtained atomically roughened Ag and Pt surfaces [22, 23].

3. Results and Discussions

Figure 2a shows the cyclic voltammogram obtained with Ag wire electrode in

the solutions of pure H_2O (broken line) and mixture of H_2O and D_2O (solid line) containing 0.5 M Na_2SO_4. This mixed ratio of H_2O and D_2O was set to 1 : 10 (about 90wt% D_2O). The shaded region in Figure 2(a) is corresponding to the redox potential of $E(H^+/H_2)$. At more negative potential corresponding to $\eta < -1.0$ V, the cathodic current gradually increased as shown in the voltammogram. As can be seen in Fig. 2a, the onset potential of the cathodic current negatively shifted about −0.1 V by the presence of D_2O. It has been reported that the difference between hydrogen and deuterium evolution was around −0.1 to −0.2 V which was derived from the different zero-point energies of the OH and OD bonding (about 1400 cal.) [25–27]. Thus, the observed negative shift of the onset potential at the D_2O mixture solution agrees with previously documented values. In order to discuss the reaction ratio of the isotopic products at large over potential (the potentials indicated as the arrows in Fig. 2a in real time, we have used the electrochemical mass spectroscopy system as illustrated in Fig. 1. Figure 2b shows the representative results of *in-situ* mass spectra obtained with the potential polarization of (solid line) −1.8 and (broken line) −1.6 V on the Ag electrode in the D_2O mixture solution. The indications of m = 2, 3, and 4 represent generated H_2, HD, and D_2, respectively. From the spectra, it was found that the ion currents for each gas product have been increasing with increasing potential polarization time. Apparently, the increment of each ion current at −1.8 V was

much larger than those at −1.6 V. This response would reflect the four times higher current density at −1.8 V than that at –1.6 V. Slight increment of ion current of D_2 at −1.6 V is due to the detection limit of the mass system. In the present manuscript, we have used the D_2O rich condition in all cases because the generated amounts of the isotopic molecules are much smaller in the case of H_2O rich condition (see details in supplementary information). As the demonstration for the high sensitivity of our system, we have also carried out repeated measurements under chronoamperometric conditions with the current at 30 mA cm^{-2} with the time intervals for 5 and 2 s as shown in Fig. 1c and d., respectively. Although there was some time delay on the evolution of the ion currents, we successfully confirmed the repetitive increments of the ion current synchronized to the chronoamperometric modulation. Typical sensitivity of *in-situ* electrochemical mass spectroscopic measurements can detect the generated compounds from electrodes in open-type cell for a few ten seconds [16,21]. Reversible response of the ion current within ten s for 2-5 s HER proves relatively high sensitivity of the present system.

As the evolved hydrogen gas, HD was detected as the dominant product even the D_2O was contained above 90% in the solution. The mechanism of HER at relatively high over potential on the surface of Ag electrode can be explained by established theory of HER [1,28–30]. Generally, at the HER from the neutral D_2O mixture solution, it can be

expected that various processes take place simultaneously. D_2O molecules are expressed by following equation in the equilibrium:

$$H_2O + D_2O \rightleftarrows 2HOD \qquad (1)$$

with the equilibrium constant of 3.8 at 25 °C.[14] At the initial step of the isotopic HER, the adsorbed hydrogen (H_{ad}) or deuterium (D_{ad}) form as following these four steps called as Volmer mechanism [31]:

$$H_2O + M + e^- \rightarrow MH_{ad} + OH^- \quad (2)$$

$$HDO + M + e^- \rightarrow MH_{ad} + OD^- \quad (3)$$

$$HDO + M + e^- \rightarrow MD_{ad} + OH^- \quad (4)$$

$$D_2O + M + e^- \rightarrow MD_{ad} + OD^- \quad (5)$$

where M is the metal atom of the surface. After these adsorption processes, the electrochemical desorption steps lead the generations of the HD, H_2, or D_2 by the below mechanisms [14,31]:

$$H_2O + MH_{ad} + e^- \rightarrow M + H_2 + OH^- \qquad (6)$$

$$H_2O + MD_{ad} + e^- \rightarrow M + HD + OH^- \qquad (7)$$

$$HDO + MH_{ad} + e^- \rightarrow M + H_2 + OD^- \qquad (8)$$

$$HDO + MD_{ad} + e^- \rightarrow M + HD + OD^- \qquad (9)$$

$$HDO + MH_{ad} + e^- \rightarrow M + H_2 + OD^- \qquad (10)$$

$$HDO + MD_{ad} + e^- \rightarrow M + D_2 + OH^- \qquad (11)$$

$$D_2O + MH_{ad} + e^- \rightarrow M + HD + OD^- \qquad (12)$$

$$D_2O + MD_{ad} + e^- \rightarrow M + D_2 + OD^- \qquad (13)$$

In addition to these, the surface catalyzed desorption step could be on the process as below:

$$MH_{ad} + MH_{ad} \rightarrow 2M + H_2 \qquad (14)$$

$$MH_{ad} + MD_{ad} \rightarrow 2M + HD \qquad (15)$$

$$MD_{ad} + MD_{ad} \rightarrow 2M + D_2 \qquad (16)$$

However, these steps which are called Tafel mechanism could be the minor at the Ag surface. This is because that the hydrogen evolution takes place with following desorption steps (eq. 6-13), called as Heyrovsky step, under relatively high over potential condition [32]. And also it has been reported that these Tafel steps become slower under the neutral condition compared to the case for the acidic condition. Therefore, it can be determined that the reactions of eq. 7, 9, and 12 are the dominant steps at the surface of Ag kept with high over potential in the isotopic mixed solution with such high D_2O concentration. In figure 1b, the second main product is H_2, not D_2, even under such high concentration of D_2O. This can be explained the fact that the kinetics of eq. 11 and 13 are quite slow compared to those of others due to the difference redox potential of H_2O and D_2O [14].

This HER mechanism is quite unique characteristics at Ag in the solution containing relatively high concentration of D_2O.

It must be mentioned here that the following equilibrium process has the possibility for the generation of HD.

$$H_2 + HDO \rightleftarrows HD + H_2O \qquad (17)$$

However, this process has not experimentally been observed even at the highly catalytic electrode metals such as Pt reported previously [33]. Thus, it could be proposed that the HD originates via the processes of eq. 7, 9, and 12 and eq. 11 and 13 at such high over potential. From the mass spectra in Fig. 2b, we have also calculated S_D value using following equations [34].

$$S_D = \frac{\left\{\frac{2[H_2]+[HD]}{2[D_2]+[HD]}\right\}_{gas}}{\left\{\frac{[H_2O]}{[D_2O]}\right\}_{liq}} \qquad (18)$$

At −1.8 V, the calculated S_D is 10.8 which is comparable the previously reported values [6]. The previous works has been revealed that the relatively large S_D value (> 8) could be assigned to the slow electrochemical desorption mechanism (Heyrovsky mechanism) [35]. This calculated S_D value is good agreement with the fact that we have discussed above.

For further investigations of the isotopic HER process at relatively high D_2O concentration, we have examined the effects of metal species as well as that of surface

morphology. The electrochemical mass spectroscopy experiments have been carried out using Pt and Ag electrodes with smooth and roughened surfaces (Fig. 3 and 4). The surface structures of Pt and Ag were shown in Fig 3a and 4a. Apparent difference of the isotopic selectivity between the Pt and Ag electrodes is that the ion current of D_2 exceeds that of H_2 unlike the case for Ag. It has been proposed that catalytic metals such as Pt result in the acceleration of the surface catalyzed step (Tafel mechanism) (14, 15, and 16) which is derived from relatively higher Pt-H bond strength of 5.03 eV and is ten to hundred times faster than the rate for Heyrovsky mechanism [36]. Considering the high concentration of D_2O in the electrolyte solution, the present results could be reasonable because the number of M-D_{ad} at the electrode surface would be larger than that of M-H_{ad} at high over potential region. Thus, the increments in the D_2 production on Pt electrode could be considered as the acceleration of the Tafel mechanism. As the proof of this, the ratio of generated H_2 and D_2 on the Ag electrode was almost equal under the acidic conditions, where the Tafel mechanism is dominant (data were not shown). In terms of the surface roughening of Pt electrode, the increment of the surface area affects the value of the ion currents for H_2, HD, and D_2 only at relatively lower over potential (−1.6 V) corresponding to the increased current. This means that, as shown in Figure 3 (b), (c), and (d), the isotopic selectivity was not dependent on the surface morphological change.

Therefore, the surface roughness of the Pt electrode did not affect S_D showing comparable values of 7.6 for both smooth and roughened electrodes.

Very interestingly, we have successfully found that S_D for Ag electrode was dependent upon the surface morphology. The ion currents observed using smooth and roughened Ag at −2.0 V were indicated in Fig. 4(b). It is important that the amount of the generated H_2 at roughed Ag was larger than that at smooth. It must be noted that the ion currents of HD and D_2 at roughened Ag were comparable to those at smooth. This means that the characteristics of selective improvement in H_2 generation at roughened Ag were observed. The ion currents of HD and D_2 at roughened Ag were also comparable with those of smooth at relatively high over potentials. It must be also emphasized that the effect of AgCl or Cl ions originated from the electrochemical surface roughening process on the isotopic selectivity can be ignored in the present case. This is because that the residual AgCl or adsorbed Cl anions can be completely reduced and removed at more negative region than −0.9 V [37]. In addition, we have confirmed the no effect of deposited Pt particles which are dissolved from counter Pt and redeposited on working electrode via the energy dispersive X-ray spectrometry measurements (see SI). From these facts, based on the electrochemical characteristics of Ag, improvement of H_2 generation would imply the possibility that selective acceleration of the reaction

processes of eq. 6, 8, 10, or 14 at roughened electrode because the Heyrovsky mechanism is the dominant at Ag surface under the high over potential condition. In regard to eq.14, although the number of MH_{ad} was increased by the increment of the surface area, the acceleration of this process would be minor because the ion currents for HD and D_2 were always comparable to the case for the smooth electrode as mentioned above. Therefore, we could conclude the acceleration of the electrochemical desorption reaction at the surface of the roughened Ag electrode due to the surface or the environmental change during HER as discussed later.

The values of S_D at the Pt and Ag electrodes with distinct surface morphology were summarized in Figure 5. The values of S_D for smooth Ag and Pt were around 10 and 7, respectively. These values are good agreement with the previous reported data [38]. As mentioned above, the relatively higher and lower S_D values is the indication of the Heyrovsky and Tafel mechanisms, respectively. The S_D values for roughened Ag and Pt were also estimated as in Fig. 5. The S_D values for the Ag electrodes increased to be 15 from 10 by the introduction of surface roughness, while those of Pt were comparable at distinct surface morphology. The present observation indicates that the process of H_2 generation in the D_2O mixture solution can be selectively accelerated at the Ag roughened electrode. This fact is interesting, because only the morphological change leads to the

increase of S_D showing such higher value. Generally, the HER activity strongly depends on the electronic structures of surfaces, such as the percentage of *d*-orbital contribution to intermetallic *d-sp* hybridized bond orbitals [13]. The present results implies that apparently similar effects on S_D modulation via just only the surface roughening of non-HER catalytic metal.

At the present stage, the origin of the S_D modulation is not clear. There are various report about the morphological effect on the multiple reaction steps, such as the selectively of CO_2 reduction. In such reports, it has been discussed that the local pH rising at the nano-structuring surface can suppress the HER and accelerate CO_2 reduction [39–42]. Taking into consideration of the high current density on the present roughened Ag surface, the local pH at the roughened surface would raise up to almost 10 [41]. Under such basic condition, it could be expected that the HER process is entirely suppressed so the relatively faster step (eq. 6, 8, or 10) would become much dominant. It should be noteworthy that the S_D modulation due to the roughening was also confirmed in the basic solution. This means that not only the local pH effect but also other factors, such as the formation of novel active sites at the very limited region which contribute to the present phenomenon as similar to the morphological effect on the CO_2 reduction reaction [43,44]. Although further investigations including both experimental and theoretical approached

are required, in-situ EC-mass measurements make possible to discuss the relationship between the isotopic reactivity and the catalytic activity for the creation of novel HER active metal electrodes.

4. Conclusion

The *in-situ* electrochemical mass spectral measurements have successfully been established through our attempts. By using this system, the detail isotope effect on Pt and Ag electrodes has been investigated based on the real time detection of generated reaction products. As the important facts obtained in the present investigations, only the surface roughening process could modulate the isotopic reaction selectivity. This could be originated from the local environmental change, such as the increment of the pH values or the formation of the catalytic site, at the nano-structured Ag surface. We now believe that this new findings would lead to the various techniques, for example the high efficient D_2O condensation method. Consequently, we are sure that the real time observation of the isotopic reaction products would provide us quite new fact against the various isotopic electrochemical reactions as demonstrated in present paper.

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Figure.

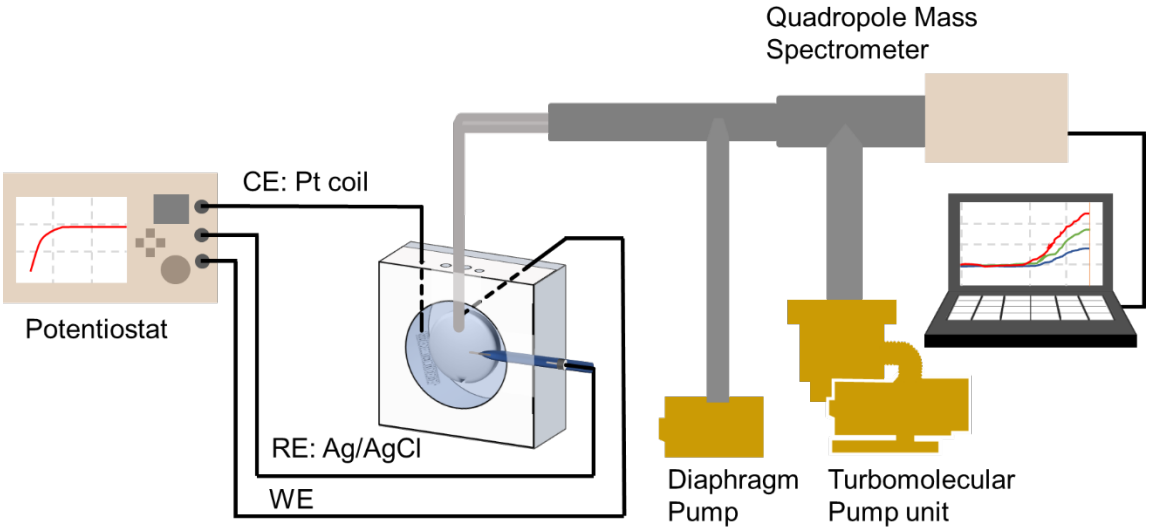

Fig. 1 | Schematic illustration of *in-situ* electrochemical mass spectroscopy system.

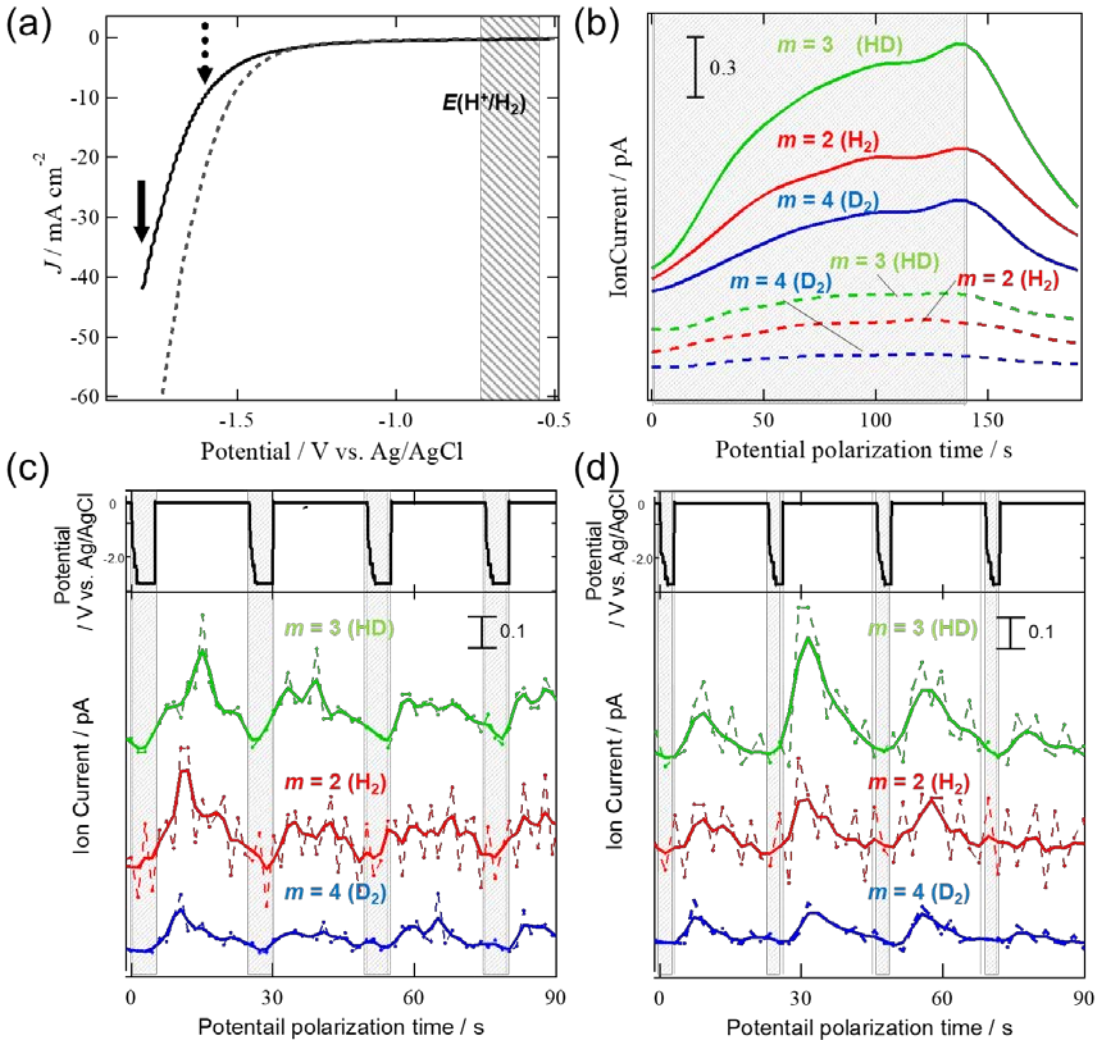

Fig. 2 | (a) Cyclic voltammograms for Ag electrode in 0.5 M Na_2SO_4 aqueous solutions. The broken and solid lines are obtained in the solution of pure H2O and mixed H_2O / D_2O, respectively. (b) Electrochemical mass spectra obtained at potential polarization of (broken) −1.6 and (solid) −1.8 V, respectively. The potential was applied for 140 s as indicated as the shadow region. (c and d) Mass spectra obtained with repeated chronoamperometric measurements. The intervals for HER was (c) 5 and (d) 2 sec, respectively.

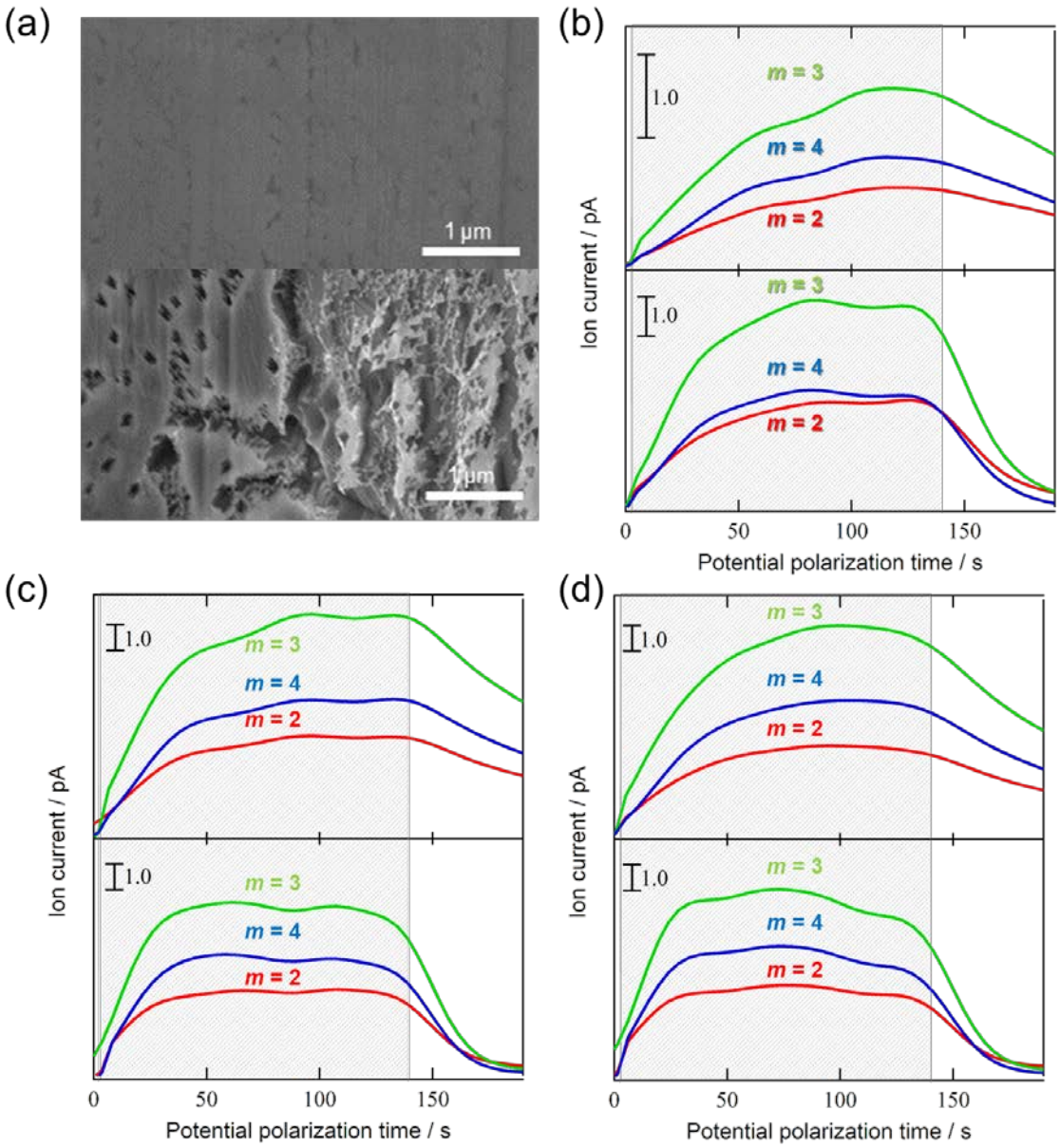

Fig. 3 | (a) SEM images of (upper) smooth and (bottom) roughened Pt surface. (b-d) Electrochemical mass spectra obtained with (upper) smooth and (bottom) roughened Pt electrodes in the mixed solution of H_2O and D_2O. The applied electrode potentials were (b) −1.6, (c) −1.8, and (d) −2.0 V, respectively.

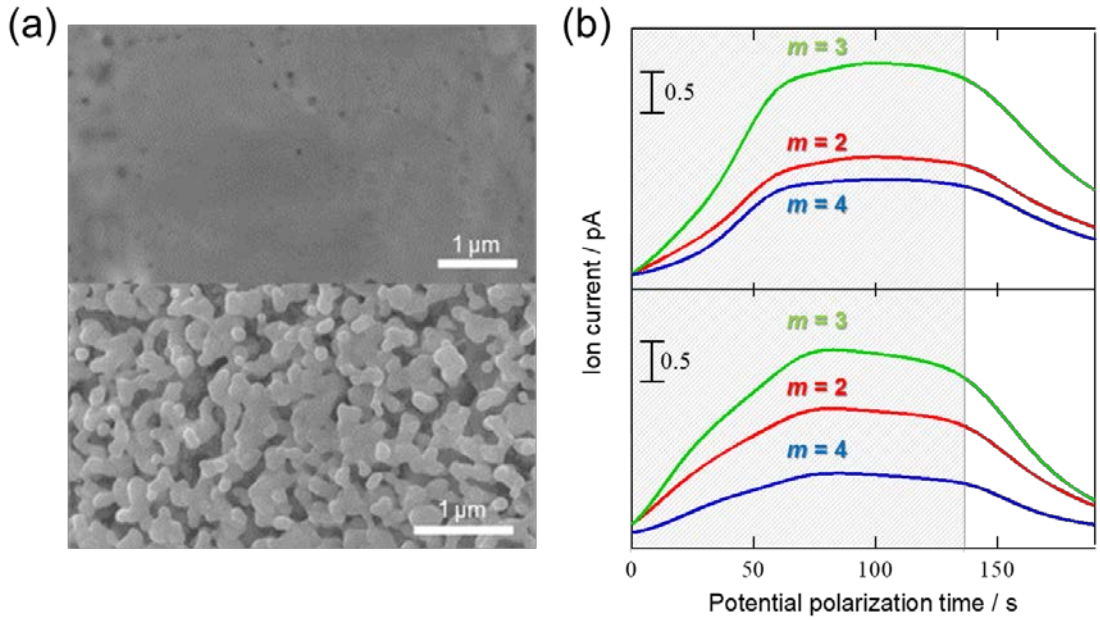

Fig. 4 | (a) SEM images of (upper) smooth and (bottom) roughened Ag surface. (b) Electrochemical mass spectra obtained with (upper) smooth and (bottom) roughened Ag electrodes in the mixed solution of H_2O and D_2O. The electrode potential was set to −2.0 V.

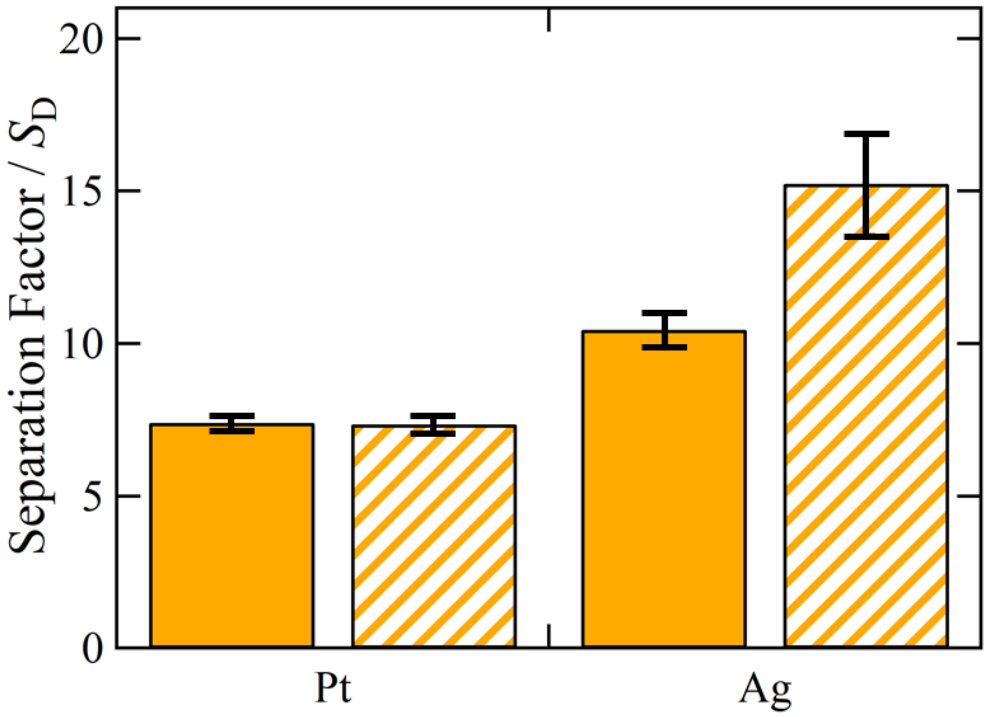

Fig. 5 | The S_D values at −2.0 V for Pt and Ag electrodes. Each shaded graph indicates the roughened Pt and Ag electrodes.