Spontaneous Motion of a Nitrobenzene Droplet on Au Electrode during Sn Electrodeposition

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The spontaneous motion of a nitrobenzene droplet on an Au electrode during an Sn electrodeposition has been reported in a previous paper (ChemPhysChem, 9, 2302 (2008)). It also mentions that the velocity of the motion increases with a negative shift in the electrode potential. This present work has studied the motive force inducing the droplet motion, which is the imbalance between interfacial tension acting on the opposite side of a nitrobenzene droplet. As explained in the previous study, a high interfacial tension on the front side of the droplet is caused by an occurrence of electrodeposition. From this study, a low interfacial tension on the rear side has been found to attribute to an occurrence of hydrogen evolution reaction on the electrode surface. The rate of hydrogen evolution reaction increases as the electrode potential decreases, and thus the increase in the droplet velocity with a decreasing potential can be ascribed to the increase in the rate of hydrogen evolution reaction. The present work also reports that the velocity also increases by the addition of a salt such as K$_2$SO$_4$ to the solutions.

On the other hand, the spontaneous droplet motion also occurs on homogeneous surface. One of the factors causing the motion is a surface tension-driven flow due to thermal or concentration gradients, which has long been known as Marangoni effects. The other factor is inhomogeneity of interfacial tension which is created dynamically by chemical reactions and/or transportation of molecules between the droplet and surface. These spontaneous motions of droplets have been of interest from the view point of direct energy conversion of chemical energy to mechanical one.

Furthermore, Nakaniishi et al. reported that the contact angle of an oil droplet put on an Au electrode surface decreased during electrodeposition of metals, such as Sn, Pb and Sb. They also reported that the droplet moved spontaneously during the electrodeposition due to the difference in $\gamma_{SW}$ between the front and rear sides of the droplet (see, Figure 1b). The motion was interesting because it was induced by simple electrochemical reactions. However, the mechanism of the motion was not fully elucidated because the difference in $\gamma_{SW}$ was little focused on in their study. This present work, then, studies the factors causing the difference and discusses the mechanism of the motion.

The droplet motion during the electrodeposition has a unique feature, which facilitates to control the motion: the velocity of the motion

Wetting properties of solid surfaces are of interest from the viewpoint of interaction between liquid and solid phases. They play important roles not only in industrial processes but also in human activities. The wettability of a solid surface can be characterized by the contact angle of a liquid droplet on the solid surface. Figure 1 illustrates cross sections of oil droplets placed on solid surfaces in water (aqueous) phases. The contact angle of the droplet ($\theta$) is defined by the mechanical equilibrium at the interface under the action of three interfacial tension (see Figure 1a), i.e., interfacial tension of solid-water interface ($\gamma_{SW}$), that of the solid-oil interface ($\gamma_{SO}$), and that of the oil-water interface ($\gamma_{OW}$), as expressed in the following Young's equation.

$$\gamma_{SW} = \gamma_{SO} + \gamma_{OW} \cos \theta$$

Comprehensive studies have demonstrated that a liquid droplet on a solid surface moves spontaneously due to an imbalance of interfacial tension acting on the droplet, as summarized in literatures. As for an oil droplet on a solid surface in a water phase, the difference of $\gamma_{SW}$ between the front and rear sides of the droplet generates a driving force for the droplet to move spontaneously in the direction of a high interfacial tension, i.e., toward the region of higher wettability, as illustrated in Figure 1b.

In the early 1990s, Ondarçuhu and Veysseye studied the behavior of a liquid droplet that was deposited on a boundary line between hydrophilic and hydrophobic parts of a plate. The droplet moved spontaneously toward the region of higher wettability, and then stopped when the rear side of the droplet reached the boundary line. Chaudhury and Whitesides reported a spontaneous droplet motion induced by a wettability gradient on a solid surface. They generated a surface-chemical gradient on a silicon wafer surface by exposing it to the diffusing front of a vapor of decyltrichlorosilane.

Since their studies were reported, not only the droplet motions due to surface-chemical gradients but also those due to morphological gradients have been extensively studied and many different methods generating wettability gradients have been developed. The droplet motions induced by wettability gradients have a merit that they do not require any power source, while they have a demerit that the production of wettability gradient surface is often sophisticated and/or costly: the production usually requires such specialized techniques as self-assembled monolayer, polymer, lithography, and electrochemical etching.

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The droplet motion during the electrodeposition has a unique feature, which facilitates to control the motion: the velocity of the motion
increased with a decreasing electrode potential.\(^{30}\) The present work, then, studies the reason for the velocity increase, and also mentions that the droplet motion can be switched on, off and back on again, which is another unique feature of the motion. These features arise because electrochemical reactions have an advantage that reaction rates can be tuned by changing the electrode potential. We therefore believe that electrochemical systems offer a good way to manipulate droplets, and then an effect of K\(_2\)SO\(_4\), which is widely used as a supporting electrolyte for electrochemical reactions, on the velocity is also studied in this work.

**Experimental**

A nitrobenzene droplet of 1 \(\mu\)L in volume was placed on an Au electrode surface (see Figure 2). The motion of the droplet was observed by CCD cameras during an Sn electrodeposition in 0.5 M H\(_2\)SO\(_4\) + 0.01 M SnSO\(_4\) at room temperature (around 25°C). The surface of the electrode was observed by using an optical microscope (Keyence, VH-5000) after the electrodeposition. All the aqueous solutions were prepared using special analytical grade chemicals (Wako Pure Chemical Industries) and purified water (Milli-Q water). A nitrobenzene droplet of 1 \(\mu\)L in volume was placed on an Au ring or plate electrode facing upward.

When 0.01 M SnSO\(_4\) was added to the H\(_2\)SO\(_4\) solution, the electrodeposition of Sn on Au electrode was studied at potentials above −0.67 V to prevent from the HER on Sn. When 0.01 M SnSO\(_4\) was added to the H\(_2\)SO\(_4\) solution, the electrodeposition of Sn, i.e., the reduction of Sn\(^{2+}\) (Sn\(^{2+}\) + 2 e\(^-\) → Sn), occurred at around −0.3 V on the Au wire electrode (Figure 3c). The Sn electrodeposition was not accompanied with the HER, indicating that the electrode surface was completely covered with the deposited Sn, and hence the reduction current observed between −0.3 and −0.66 V was attributed to the Sn electrodeposition. During the Sn electrodeposition, the current was almost constant between ca. −0.3 and −0.66 V. When E was held at values between them for several tens of minutes, Sn dendrites were formed on the electrode surface (data not shown). It is known that dendrites are formed on an electrode surface during an electrodeposition when it is performed under the conditions that the transport of metal ions to the electrode is the

**Results and Discussion**

**Electrochemical measurements.**—Figure 3 shows the \(I – E\) curves for the Au and Sn wire electrodes in 0.5 M H\(_2\)SO\(_4\) with or without 0.01 M SnSO\(_4\). The curves were obtained when \(E\) was scanned in the negative direction. In the absence of SnSO\(_4\), the hydrogen evolution reaction (HER) due to the reduction of H\(^+\) (2 H\(^+\) + 2 e\(^-\) → H\(_2\)) on Au started to occur at around −0.1 V, as shown in the inset of Figure 3a, which was in good agreement with a literature value.\(^{31}\) The reduction current due to the HER increased (in absolute value) with the decreasing potential (Figure 3a), and hydrogen bubbles were observed on the electrode surface in the potential region below ca. −0.4 V. On the other hand, the HER on Sn was not active compared with Au,\(^{32,33}\) and it started to occur at ca. −0.67 V, as shown in the inset of Figure 3b. Therefore, in the following experiments, the electrodeposition of Sn on Au electrode was studied at potentials above −0.67 V to prevent from the HER on Sn.
rate-limiting step. Therefore, we can say that the Sn reduction was limited by the diffusion transport of Sn\(^{2+}\) to the electrode surface at \(-0.40 \text{ V}\) or lower.

The Sn electrodeposition also occurred on the Au plate electrodes, namely the Au ribbon and disc electrodes, below ca. \(-0.3 \text{ V}\), as shown in Figure 4a for the Au ribbon electrode. In contrast to the case of the Au wire electrode, the electrodeposition was accompanied with the hydrogen bubble evolution in the potential region below ca. \(-0.4 \text{ V}\), and the reduction current increased (in absolute value) with the decreasing potential until around \(-0.45 \text{ V}\). These results indicate that the surfaces of the Au plate electrodes were not completely covered with the deposited Sn during the electrodeposition. This was probably because the transport rate by the Sn\(^{2+}\) diffusion to the surfaces was slow compared with the Au wire electrode.

Incidentally, the apparent current density during the electrodeposition for the Au plate electrodes, e.g., \(-0.016 \text{ mA mm}^{-2}\) at \(-0.6 \text{ V}\), was smaller (in absolute value) than that for the Au wire electrode (the surface area of which was ca. \(6.5 \text{ mm}^2\)), e.g., \(-0.025 \text{ mA mm}^{-2}\) at \(-0.6 \text{ V}\). This supports that the transport rate of the Sn\(^{2+}\) diffusion to the Au plate electrode was slower than that to the Au wire electrode.

As mentioned above, Sn dendrites were formed on the Au wire surface at \(-0.40 \text{ V}\) or lower. The dendrite formation was also observed on the Au plate electrodes, e.g., at \(-0.66 \text{ and } -0.40 \text{ V}\) as shown in Figures 4b and 4c. On the other hand, after the electrodeposition at \(-0.35 \text{ V}\), Sn dendrites were not observed on the Au plate electrodes, as shown in Figure 4d. These results clearly show that the Sn reduction on the Au plate electrode was also limited by the diffusion transport of Sn\(^{2+}\) at \(-0.40 \text{ V}\) or lower.

**Spontaneous motion of droplets.** As mentioned in the Introduction, it was reported that the contact angle of an oil droplet on an Au electrode decreased and the droplet moved during Sn electrodeposition. We, then, observed the droplet on the Au disc electrode in 0.5 M H\(_2\)SO\(_4\) + 0.01 M SnSO\(_4\). The contact angle decreased and the droplet moved, when \(E\) was stepped to potentials more negative than \(-0.41 \text{ V}\), where hydrogen bubbles evolved from the Au disc electrode during the Sn electrodeposition.

Figure 5 shows the time course of \(E\) and \(I\) when \(E\) was stepped to \(-0.66 \text{ V}\) from the rest potential (about 0.3 V) at \(t = 0 \text{ s}\) and the snapshots of the droplet. The current increased (in absolute value) suddenly when \(E\) was stepped, and then decayed with time owing to a decrease in the concentration of Sn\(^{2+}\) at the electrode surface (Figures 5a and 5b). The contact angle decreased immediately after the potential step due to the Sn electrodeposition (Figure 5c). At \(t = 5 \text{ s}\), hydrogen bubbles started to evolve from the electrode surface. Then, at \(t = 8 \text{ s}\), the angle decrease stopped and the droplet started to move (Figure 5d).

The time at which the droplet started to move fluctuated between 2 and 10 s, which was probably due to the difference in the surface roughness. However, the droplet started to move usually within a few seconds after the bubble evolution was observed. Similarly to the results reported previously, once the motion started, it continued for several minutes until the droplet got stuck at deposited projections.
As mentioned in the previous paper, the velocity of the motion increased as \( E \) decreased. We, then, measured the velocity by using the Au ring electrode because the droplet moved in one direction along the ring (see Figure 9). Figure 6 plots the velocity against \( E \). The velocity was zero at \(-0.41\) V or higher even if the Sn electrodeposition occurred, whereas it increased as \( E \) decreased below \(-0.41\) V; around \(0.13\) mm s\(^{-1}\) at \(-0.46\) V or \(-0.56\) V, and \(0.23\) mm s\(^{-1}\) at \(-0.66\) V.

The velocity could be tuned by changing \( E \). Moreover, the droplet motion could be switched off and on again in the following manner. The motion stopped if \( E \) was stepped to \(-0.41\) V or higher, and then restarted if \( E \) was returned to a potential below \(-0.41\) V. This indicates that the motion can be controlled arbitrarily by changing \( E \).

**Role of the HER.** As shown above, the Sn electrodeposition on the Au plate electrodes occurred in the potential region below \(-0.3\) V, and it was accompanied with the hydrogen bubble evolution below \( ca. -0.4 V \). The droplet moved when \( E \) was stepped to potentials more negative than \(-0.41\) V, and thus it was natural that not only the electrodeposition but also the HER played an important role for the droplet motion.

To study the role of the HER for the motion, the droplet motion was repetitively observed (over 100 times) at a potential, e.g., \(-0.66\) V, where the hydrogen bubble evolution was observed clearly during the Sn electrodeposition on the Au plate electrodes. It was always observed that the bubbles evolved on the electrode surface near the rear side of the droplet. Some of them were often close or attached to the rear side (Figure 7a). On the other hand, almost no bubbles were observed near the front side of the droplet. Therefore, we can conclude that the HER occurred vigorously near the rear side compared with the front side.

It was possible that the bubbles attached to the rear side pushed the droplet. However, this possibility was eliminated because the droplet moved even when the bubbles evolved at a slight distance from the rear side (Figure 7b).

**Mechanism of the motion.** According to the previous study, the role of the Sn electrodeposition for the motion can be explained as follows. The solid-water interfacial tension \( \gamma_{SW} \) during the electrodeposition is large compared with that in the absence of the electrodeposition because reaction intermediates of the electrodeposition, namely Sn adatoms on the electrode surface, increases \( \gamma_{SW} \). The droplet moves because \( \gamma_{SW} \) at the front side of the droplet \( (\gamma_{SW}^f) \) is higher than \( \gamma_{SW} \) at the rear side \( (\gamma_{SW}^r) \), as explained in the Introduction (see Figure 1b). Based on the above results, we can propose that \( \gamma_{SW}^f \) became lower than \( \gamma_{SW}^r \) due to the occurrence of the HER at the rear side, as illustrated in Figure 8. The difference between \( \gamma_{SW}^f \) and \( \gamma_{SW}^r \) can be explained by an assumption that the HER partially suppresses the Sn electrodeposition. An efficient occurrence of electrodeposition without the HER results in a high density of Sn adatoms, leading to a high \( \gamma_{SW} \) on the front side, while the suppression of the electrodeposition due to the HER results in a low density of adatoms, leading to a low \( \gamma_{SW} \) on the rear side.

Now, let us consider the dependence of the droplet velocity on \( E \). The velocity increases as \( E \) decreases below \(-0.41\) V (see Figure 6). In the potential region below \(-0.41\) V, the density of Sn adatoms, which is determined by the rate of electrodeposition, is constant at the front side because the Sn electrodeposition is limited by the mass-transport of Sn\(^2\)\(^+\) ions to the electrode surface (shown by Figure 4). We can thus conclude that \( \gamma_{SW}^f \) is constant independently of \( E \) in the potential region where the droplet moves. Hence, the velocity increase is attributed to a decrease in \( \gamma_{SW}^f \) with a negative shift in \( E \) because it is caused by the increase in the driving force for the motion, namely by the increase in the difference between \( \gamma_{SW}^f \) (a constant value) and \( \gamma_{SW}^r \). As \( E \) decreases, the density of Sn adatoms at the rear side decreases because the HER rate increases, and consequently \( \gamma_{SW}^r \) decreases with the negative shift in \( E \). The turn on/off of the motion can also be explained by the dependence of the HER rate on \( E \).

**Suppression of the Sn electrodeposition due to HER.** In order to verify the assumption concerning the suppression of the Sn electrodeposition by the HER, the Sn electrodeposition on the Au wire electrode was studied again under the conditions that the SnSO\(_4\) concentration was kept constant at 0.01 M while the H\(_2\)SO\(_4\) concentration was varied from 0.1 M to 0.5 M. In the acidic solutions, 0.01 M SnSO\(_4\) was dissolved, and thus the solutions were colorless and transparent. When the H\(_2\)SO\(_4\) concentration was 0.1 M (the pH of the solution was 1.0), a white precipitate was observed in the solution, i.e., the initial transparent solution became cloudy, after the Sn electrodeposition at \(-0.66\) V for 300 s. On the other hand, when the H\(_2\)SO\(_4\) concentration was 0.2 M or higher (i.e., the pH was ca. 0.7 or less), the precipitate was not observed in the solution, that is, the solution remained colorless and transparent after the Sn electrodeposition.

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**Figure 6.** Dependence of droplet velocity on \( E \) measured for an Au ring electrode. The solution is 0.5 M H\(_2\)SO\(_4\) + 0.01 M SnSO\(_4\).

**Figure 7.** Snapshots from the top of the droplet in 0.5 M H\(_2\)SO\(_4\) + 0.01 M SnSO\(_4\). Hydrogen bubbles were observed (a) close to the rear side and (b) at a slight distant from the rear side. The potential is stepped to \(-0.66\) V from 0.3 V at \( t = 0 \) s. The working electrode is (a) Au ribbon of 3 mm × 10 mm and (b) Au disc of 10 mm in diameter.

**Figure 8.** A schematic illustration of the mechanism of the spontaneous motion.
The precipitate was thought to be tin (II) hydroxide, Sn(OH)$_2$, and thus the formation of Sn(OH)$_2$ should occur when the pH was higher than 1.1 for 0.01 M Sn$^{2+}$, according to the solubility product of Sn(OH)$_2$ ($K_{sp} = [\text{Sn}^{2+}][\text{OH}^-]^2 = 1.4 \times 10^{-25}$ (mol/l)$^3$). However, the formation was observed in the 0.1 M H$_2$SO$_4$ solution during the Sn electrodeposition, indicating that the local pH at the electrode surface became higher than 1.1 during the Sn electrodeposition. This was because the HER occurred during the electrodeposition and it led to the increase in the local pH as a consequence of H$^+$ consumption, as is generally known in electrodeposition processes.\textsuperscript{35}

According to the literature,\textsuperscript{35} it is also known that the pH value at the electrode surface can differ from that of the bulk by several pH units, and that the pH increase due to the HER results eventually in metal hydroxide precipitation. Thus, Sn(OH)$_2$ should be formed within a diffusion layer of H$^+$ ions even at the 0.5 M H$_2$SO$_4$ solution (the pH was ca. 0.4), though no precipitate was visible in the solution. This was probably because the precipitate dissolved when it diffused out of the diffusion layer.

The above assumption can thus be justified by taking into account a formation of Sn(OH)$_2$. In the rear side of the droplet, the local pH at the electrode surface increases because the HER consumes H$^+$ ions, and hence Sn(OH)$_2$ is formed at the surface. The surface concentration of Sn$^{2+}$ ions thus becomes lower in the rear side than the front side, and as a result, the rate of Sn electrodeposition becomes slower in the rear side than the front side. This is the origin of the difference between $\gamma_{SWr}$ and $\gamma_{SWf}$.

As $E$ decreases, the rate of the Sn(OH)$_2$ formation in the rear side increases due to the increase in the rate of the HER, which is supported by the experimental fact that the rate of the precipitate formation became faster with the negative shift in $E$, and as a result, the rate of Sn electrodeposition in the rear side decreases. This is why $\gamma_{SWf}$ decreases with the negative shift in $E$.

Increase in the velocity in the presence of salts. — As shown above, the velocity of the droplet motion increased as $E$ decreased. Moreover, the velocity was found to increase by the addition of K$_2$SO$_4$ to the solutions. Figure 9 shows the effect of K$_2$SO$_4$ on the velocity during the electrodeposition at $-0.66$ V. The velocity increased almost linearly as the K$_2$SO$_4$ concentration increased. This result indicates that the driving force, $\gamma_{SW} - \gamma_{SWf}$, increased with the increasing K$_2$SO$_4$ concentration. We can thus say that the salt caused the increase in $\gamma_{SW}$ and/or the decrease in $\gamma_{SWf}$, the latter of which can be justified by considering the effect of K$^+$ ions on the rate of HER as below.

The local pH at the electrode surface during the HER is higher in the presence of K$_2$SO$_4$ than in the absence of K$_2$SO$_4$ because K$^+$ ions diminish the electromigration transport of H$^+$ ions to the electrode surface.\textsuperscript{36,37} Therefore, the local pH at the rear side increases with the increasing K$_2$SO$_4$ concentration, which results in the decrease in $\gamma_{SWf}$. This was confirmed by the experimental fact that the formation of Sn(OH)$_2$ was observed after the Sn electrodeposition even at 0.2 M H$_2$SO$_4$ solution when 0.2 M K$_2$SO$_4$ was added to the solution. It is, thus, plausible that the salt causes the decrease in $\gamma_{SWf}$. Here, without taking into consideration the effect of K$^+$ ions on the rate of HER, let us consider the increase in the driving force with the increasing K$_2$SO$_4$ concentration. Inorganic salts including K$_2$SO$_4$ are known to increase the surface tension of water, i.e., the interfacial tension of air-water interface.\textsuperscript{38} On the analogy of this, it was possible that $\gamma_{SW}$ increased by the addition of the salt. If so, both $\gamma_{SW}$ and $\gamma_{SWf}$ increased at the same ratio by the addition of the salt. Therefore, the driving force, $\gamma_{SW} - \gamma_{SWf}$, also increased at the same ratio, leading to the velocity increase. A further study is needed to justify the increase in $\gamma_{SW}$.

Conclusions

We studied the spontaneous motion of a nitrobenzene droplet put on an Au electrode during Sn electrodeposition in an acidic solution. Repetitive observation of the motion revealed that the droplet moved when the electrodeposition was accompanied by the hydrogen evolution reaction (HER). The high interfacial tension on the front side of the droplet was caused by an efficient occurrence of the electrodeposition without the HER, whereas the low interfacial tension on the rear side was attributed to the occurrence of the HER on the rear side; the HER lowered the interfacial tension during the Sn electrodeposition.

The droplet velocity and the turn on/off of the motion could be controlled by the electrode potential because the rate of the HER depended on the electrode potential. Moreover, the velocity increased when K$_2$SO$_4$ was added to the solutions. This was probably because the interfacial tension at the rear side decreased with the increasing K$_2$SO$_4$ concentration.

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Figure 9. (a) Snapshots of droplets in 0.5 M H$_2$SO$_4$ + 0.01 M SnSO$_4$ + x M K$_2$SO$_4$ where x is varied from 0 to 0.20 M. (b) Dependence of the droplet velocity on the K$_2$SO$_4$ concentration. The potential is stepped to $-0.66$ V from about 0.25 V at $t = 0$ s.
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