Research Paper**Investigation of Spontaneous Hydrogen Evolution Using a Photochemical Reaction of Fullerene (C_{60}) by means of Voltammetry with an Electron Conductor Separating Oil-Water (ECSOW) System**

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In order to achieve the spontaneous hydrogen (H_2) evolution by using a photochemical reaction of fullerene (C_{60}), voltammetric behaviors of C_{60} and its anion radical ($C_{60}^{\cdot-}$) were investigated by means of voltammetry with an electron conductor separating oil-water (ECSOW) system. Nitrobenzene (NB) solutions and acidic aqueous solutions were used as the oil phase and the water (W) phase, respectively. In this work, two working electrodes with greatly different areas were used as the electron conductors, although two working electrodes with almost the same areas are usually used in voltammetry for the ECSOW system. As a result, we confirmed that the currents are controlled by the working electrode with a smaller area. Especially, when a microelectrode was used in the NB phase containing C_{60} or $C_{60}^{\cdot-}$, s-shaped voltammograms with limiting currents were obtained and thereby the diffusion coefficients of C_{60} and $C_{60}^{\cdot-}$ were easily estimated to be 3.2×10^{-6} and $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. On the other hand, we could determine a criterion for the spontaneous H_2 evolution from the voltammogram measured for the ECSOW system, considering that the potential of the voltammogram corresponds to the electromotive force of the voltaic cell consisting of the NB and W phases. Based on this criterion, we supposed conditions for the spontaneous H_2 evolution and successfully achieved the spontaneous H_2 evolution using a photovoltaic cell.

Introduction

So far, we have been examining a photochemical reaction of fullerene (C_{60}) in a nitrobenzene (NB) solution containing tetraphenylboate (TPB^-). In these works,¹⁾⁻³⁾ we experimentally showed that C_{60} readily reacts with TPB^- to form its anion radical ($C_{60}^{\cdot-}$) in the NB solution under artificial solar-light irradiation and that $C_{60}^{\cdot-}$ is stable at least for a week in the NB solution thoroughly deaerated with nitrogen

or argon gas. Based on this property of $C_{60}^{\cdot-}$, we have proposed a new photovoltaic cell, called a photoelectrochemical condenser (PEC).³⁾ Further, taking advantage of the principle of PEC, we attempted to generate hydrogen gas (H_2) instead of the electric power, and achieved the spontaneous H_2 evolution and reported its part promptly.⁴⁾ In the present paper, we will discuss basic voltammetric studies for the spontaneous H_2 evolution, that is, voltammetric behaviors of C_{60} and $C_{60}^{\cdot-}$ in an electron conductor separating oil-water (ECSOW) system consisting of a NB phase and a water (W) phase, and a criterion for the spontaneous H_2 evolution. Furthermore, we

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will show some states of the spontaneous H_2 evolution by artificial solar-light irradiation obtained under several conditions, using pictures.

A main chemical reaction for the H_2 evolution used in this work is $C_{60}^{\cdot-}(NB) + H^+(W) \rightarrow 1/2 H_2$. Since the standard potentials for $C_{60}(NB) + e^- \rightleftharpoons C_{60}^{\cdot-}(NB)$ and $H^+(W) + e^- \rightleftharpoons (1/2) H_2$ are reported to be -0.918 and -0.42 V vs. Fc/Fc^+ (Ferrocene/Ferricinium ion), respectively,⁵⁾⁻⁷⁾ $C_{60}^{\cdot-}(NB)$ is expected to be able to reduce $H^+(W)$ to H_2 . Based on this expectation, we first checked the spontaneous H_2 evolution by irradiating a mixture of a NB solution containing C_{60} and TPB^- , and an acidic aqueous solution with artificial solar-light. However, we could not observe the evolution. The cause of this is probably because $C_{60}^{\cdot-}$ and H^+ directly react at the NB/W interface to form some compounds other than H_2 . In order to avoid the direct contact of the NB and W solutions, we employed an electron conductor separating oil-water (ECSOW) system, in which the NB and W phases are separated with electric conductors, for example, two working electrodes and a lead wire connecting them. Although the ECSOW system was originally proposed to distinguish between ion transfer and electron transfer in voltammetry at an interface between two immiscible electrolyte solutions (ITIES),^{8), 9)} we regarded the ECSOW system as a voltaic cell consisting of the NB and W phases in the present work. Using this ECSOW system, we examined voltammetric behaviors of C_{60} and $C_{60}^{\cdot-}$ for determining conditions for the spontaneous H_2 evolution, and based on the results, we achieved the spontaneous H_2 evolution in a photovoltaic cell used for PEC.^{3),}

4)

Experimental

In the present work, we used two kinds of electrochemical cells. One was an electrolytic cell (Cell 1) shown in Fig. 1 and the other was a photovoltaic cell (Cell 2) shown in Fig. 2. Both cells consisted of two compartments for the NB and W phases. For examining the ECSOW system, an electrochemical analyzer (BAS, ALS760 D) was used in a four-electrode mode. In Cell 1, two combinations of the working electrodes were adopted. In the first combination, an Au microelectrode with a nominal diameter of $10 \mu m$ for the NB phase and a Pt spiral electrode for the W phase, as shown in Fig. 1.⁴⁾ The diameter of the microelectrode was calibrated to be $16.4 \mu m$ based on a limiting current in a linear scan voltammogram for $[Fe(CN)_6]^{4-}$ in 1.0 M ($1 M = 1 \text{ mol dm}^{-3}$) KCl.¹⁰⁾ In the second, a Pt gauze electrode with a large electrode area for the NB phase and a Pt spiral electrode for the W phase. In both combinations, the currents are expected to be controlled by the electrodes with smaller areas, that is, the microelectrode in the first combination and the Pt spiral electrode in the second. Two reference electrodes for the NB and W phases were Ag/AgCl electrodes prepared with 100 mM LiCl and 10 mM tetrapentylammonium chloride (TPACl) (RE1) and with 100 mM LiCl and 100 mM Na_2SO_4 (RE2), respectively. Counter electrodes, CE1 and CE2, were Pt spiral wires for both phases. In the voltammetric measurements with the Au microelectrode (the first combination), the NB phase contained 1.0 mM

Fig. 1. Electrolytic cell with an Au microelectrode for the ECSOW system (Cell 1 for the first combination). E1 and E2 are the Au microelectrode with a nominal diameter of 10 μm for the NB phase and the Pt spiral electrode for the W phase, respectively. RE1 is an Ag/AgCl reference electrode consisting of 100 mM LiCl and 10 mM TPACl, and RE2 is an Ag/AgCl reference electrode consisting of 100 mM LiCl and 100 mM Na₂SO₄. CE1 and CE2 are both Pt counter electrodes. The Au microelectrode and the Pt spiral electrode were joined with a lead wire. "Reprinted with permission from Ref. 4 (Copyright 2018, The Chemical Society of Japan.)"

fullerene (C₆₀) or anion radical of C₆₀ (C₆₀^{•-}) and 10 mM tetrapenthyllammonium tetraphenylborate (TPATPB) serving as a supporting electrolyte and the W phase contained 100 mM Na₂SO₄ or 50 mM sulfuric acid (H₂SO₄) and 100 mM Na₂SO₄. Both phases were thoroughly deaerated by bubbling with argon gas. The anion radical of C₆₀ was prepared before each voltammetric measurement by irradiating the NB phase with artificial solar-light emitted from a Xe lamp (Asahi Bunkou, LAX-C100) for approximately 1 hour in order to convert C₆₀ to C₆₀^{•-} in a simple

Fig. 2. Photovoltaic cell consisting of the NB and W phases (Cell 2). A Pt mesh electrode and a Pt spiral electrode were used for the NB and W phases, respectively. The NB phase was irradiated with artificial solar light. "Reprinted with permission from Ref. 4 (Copyright 2018, The Chemical Society of Japan.)"

grove box. The conversion was confirmed by measuring a Vis/NIR absorption spectrum of C₆₀^{•-} by using a spectrophotometer (JASCO, V-670).¹⁾ The potential of a linear scan voltammogram, ΔE , is a potential difference between the potential of the W phase, E_W , and that of the NB phase, E_{NB} , that is, $\Delta E = E_W - E_{NB}$. Further, the positive currents indicate that electrons are transferred from the NB phase to the W phase and *vice versa*. The voltammograms were usually measured at the scan rate of 5 mVs⁻¹. On the other hand, Cell 2 (Fig. 2) was a photovoltaic cell and used for the H₂ evolution.⁴⁾ The cell consisted of two compartments for the NB and W phases. The compartment for the NB phase was a rectangular glass vessel and the artificial solar-light was introduced from the front plane of the vessel. The NB phase contained 1.0 mM C₆₀, 100 mM TPATPB, and 100 mM tetrabutylammonium perchlorate (TBAClO₄).

Fig. 3. Linear scan voltammograms for C_{60} (a) and $C_{60}^{\bullet-}$ (b) in the ECSOW system. The concentrations of C_{60} and $C_{60}^{\bullet-}$ were 1.0 mM. The supporting electrolytes were 10 mM TPATPB for the NB phase, and 0 or 50 mM H_2SO_4 and 100 mM Na_2SO_4 for the W phase. The potential was scanned from the negative potential side at 5 mVs^{-1} .

The reason why $TBAClO_4$ was added in the NB phase is for improving the electric conductivity of the NB phase. Various concentrations of hydrochloric acid (HCl) and/or perchloric acid ($HClO_4$) were used as the W phase. The H_2 evolution was checked with a portable hydrogen-gas detector (TOKA SEIKI CO., LTD., Model TIP-HY), which is one of amperometric gas sensors.

Results and Discussion

Linear scan voltammograms obtained by using Cell 1 with the Au microelectrode for the NB phase and the Pt spiral electrode for the W phase (the first combination)

First, we measured linear scan voltammograms, putting the Au microelectrode into the NB phase of Cell 1. The calibrated diameter of the

microelectrode was $16.4\text{ }\mu\text{m}$, as previously mentioned. In these measurements, both the NB and W phases were thoroughly deaerated by bubbling with argon gas. Figures 3(a) and 3(b) show the voltammograms for C_{60} and $C_{60}^{\bullet-}$, respectively. The anion radical of C_{60} was prepared by irradiating the NB phase containing C_{60} with the artificial solar-light. As can be seen in the voltammograms in Fig. 3(a), the negative wave with the limiting current was observed regardless of the presence of sulfuric acid (H_2SO_4). According to the definition, the negative currents are due to the electron transfer from the W phase to the NB phase. Since the electrode reaction on the Au microelectrode in the NB phase is expected to be responsible for the wave, it is reasonable that C_{60} is reduced to $C_{60}^{\bullet-}$ on the microelectrode in the NB phase. In connection, the diffusion coefficient of C_{60} was estimated to be $3.2 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ from the limiting current, and this value agreed well with a literature value of $3.2 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$.^{11), 12)} However, it is not clear what substances are oxidized on the Pt spiral electrode in the W phase. It is likely in this case that H_2O is oxidized to O_2 or H_2O_2 on the Pt spiral electrode in the W phase. Indeed, the wave was shifted to the negative potential region when H_2SO_4 was added, indicating that H_2O becomes difficult to be oxidized as the concentration of H^+ is increased. On the other hand, the positive waves were observed in the voltammograms, as shown in Fig. 3(b). These positive waves showed a somewhat unfavorable shape compared to the negative waves in Fig. 3(a), that is, the limiting current slowly increased with the potential, and moreover a part of the currents became

negative instead of zero in the negative potential region. These unfavorable aspects would be ascribed to the incomplete conversion of C_{60} to $C_{60}^{\bullet-}$ and byproducts produced when $C_{60}^{\bullet-}$ was prepared by the irradiation.²⁾ Nevertheless, since the positive currents indicate the electron transfer from the NB phase to the W phase, it is reasonable that the wave is mainly due to oxidation of $C_{60}^{\bullet-}$ to C_{60} . In addition, even when the voltammetric measurements were performed by using HCl instead of H_2SO_4 in the W phase, the voltammograms shown in Fig. 3(b) changed very little, implying that the voltammograms are not directly concerned with kinds of acids contained in the W phase. The log-plot analysis of the voltammogram for the W phase containing 50 mM H_2SO_4 shown in Fig. 3(b) showed a straight line in the potential region between -0.82 and -0.87 V with the slope of 56 mV and the half-wave potential of -0.848 V, indicating that the electrode reaction is a reversible one-electron process. A dependence of the limiting current, I_l , on a concentration of $C_{60}^{\bullet-}$ was linear with the correlation coefficient, R , of 0.992 in the concentration range from 0 to 0.8 mM, that is,

$$I_l(\text{nA}) = 0.623 \text{ nA/mM} \times [C_{60}^{\bullet-}](\text{mM}) + 0.057 \text{ nA}.$$

The diffusion coefficient of $C_{60}^{\bullet-}$ estimated from the limiting current was $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is slightly smaller than that of C_{60} . These facts strongly support that the positive waves are due to oxidation of $C_{60}^{\bullet-}$ to C_{60} . However, it is uncertain what substances are reduced on the Pt spiral electrode in the W phase. Hydrogen ion (H^+) and H_2O are possible candidates to be reduced. In fact, the positive wave shifted to the negative potential region by adding H_2SO_4 . Although the H_2 evolution was expected from

Fig. 4. Linear scan voltammograms for $C_{60}^{\bullet-}$ in the ECSOW system consisting of the NB and W phases. (i) The NB phase contained no $C_{60}^{\bullet-}$ and 10 mM TPATPB as a supporting electrolyte, and the W phase 100 mM LiCl and 1.0 M HCl. (ii) The NB phase contained 1.0 mM $C_{60}^{\bullet-}$ and 10 mM TPATPB, and the W phase 100 mM LiCl. (iii), (iv), and (v) All the NB phases contained 1.0 mM $C_{60}^{\bullet-}$ and 10 mM TPATPB as a supporting electrolyte, and the W phase 100 mM LiCl and 1.0, 5.0, and 11.4 M HCl, respectively. The potential was swept from negative to positive at 10 mVs^{-1} . "Reprinted with permission from Ref. 4 (Copyright 2018, The Chemical Society of Japan.)"

these results, we could not confirm the H_2 evolution on the Pt spiral electrode by the naked eye in these experiments. We will discuss the H_2 evolution in detail in the following section.

Linear scan voltammograms obtained by using Cell I with the Pt gauze electrode for the NB phase and the Pt spiral electrode for the W phase (the second combination)

The voltammetric measurements using the Au microelectrode certainly showed that $C_{60}^{\bullet-}$ is oxidized to C_{60} in the NB phase. However, it remains unclear what species are reduced and produced on the Pt spiral electrode in the W phase. In order to reveal these questions, we carried out voltammetric measurements, using a Pt gauze electrode with a large area for the NB phase and

the Pt spiral electrode for the W phase. The use of the Pt gauze electrode for the NB phase allows to increase the current due to oxidation of $C_{60}^{\cdot-}$ to C_{60} and consequently it becomes easy to examine what species are reduced on the Pt spiral electrode in the W phase. For these measurements, we modified Cell 1 in size so that the Pt gauze electrode with a diameter of approximately 45 mm was adequately contained in the compartment for the NB phase. Both phases were thoroughly deaerated by bubbling with argon gas in a similar manner to the previous measurements with the Au microelectrode for the NB phase. Figure 4 shows the voltammograms for the ECSOW system consisting of the NB phase containing 1.0 mM $C_{60}^{\cdot-}$ and the W phase containing various concentrations of HCl.⁴⁾ The final discharge in the positive potential region indicates oxidation of $C_{60}^{\cdot-}$ on the Pt gauze electrode in the NB phase. At the same time, H^+ is reduced to H_2 on the Pt electrode in the W phase, as shown later. In the absence of $C_{60}^{\cdot-}$ in the NB phase {the voltammogram (i)}, the final discharge appeared in the very positive potential region with a shoulder wave around 0.4 V. This fact implies that another species, for example, $TPB^{\cdot-}$ is oxidized on the Pt gauze electrode in the NB phase and H_2O is reduced to H_2 in the W phase. On the other hand, the final discharge in the negative potential region would be due to reduction of NB serving as the solvent on the Pt gauze electrode and oxidation of H_2O on the Pt spiral electrode, which are thought to occur simultaneously. In the presence of $C_{60}^{\cdot-}$ in the NB phase {the voltammograms from (ii) to (v)}, as the concentration of HCl was increased, the positive final discharge shifted to the negative direction and attained to the negative potentials at

the concentrations of HCl more than 5.0 M, whereas the negative final discharge shifted to the positive direction. In addition to the negative final discharge, the negative wave appeared before the negative final discharge with increasing concentration of HCl. This wave is probably due to reduction of C_{60} regenerated from $C_{60}^{\cdot-}$. However, we did not examine these complicated changes with the concentration of HCl in detail anymore in this work.

Here, considering this ECSOW system to be a voltaic cell, we can express the system as follows:

Pt gauze electrode | $C_{60}^{\cdot-}$, C_{60} (NB) || H^+ , Cl^- (W) | H_2 (gas) | Pt spiral electrode.

The total reaction of this cell is

The electrochemical force, E_{emf} ($= E_{H^+/H_2(\text{W})} - E_{C_{60}/C_{60}^{\cdot-}(\text{NB})}$), is expressed as

$$E_{\text{emf}} = E^\circ - \frac{RT}{F} \ln \frac{(p_{H_2})^{1/2} a_{C_{60}(\text{NB})}}{a_{H^+(\text{W})} a_{C_{60}^{\cdot-}(\text{NB})}}. \quad (2)$$

Here, $E^\circ = E_{H^+/H_2(\text{W})}^\circ - E_{C_{60}/C_{60}^{\cdot-}(\text{NB})}^\circ$, when

$E_{H^+/H_2(\text{W})}^\circ$ and $E_{C_{60}/C_{60}^{\cdot-}(\text{NB})}^\circ$ denote the standard potentials of the redoxes of $H^+ + e^- \rightleftharpoons (1/2)H_2$ in the W phase and $C_{60} + e^- \rightleftharpoons C_{60}^{\cdot-}$ in the NB phase, respectively. The symbols R , T , and F are the gas constant, the temperature, and the Faraday constant, respectively. The symbols of a and p indicate the activity and the pressure, respectively. On the other hand, the potential of the voltammogram, $\Delta E (= E_W - E_{\text{NB}})$, is the potential

of the W phase referring to that of the NB phase, that is,

$$\Delta E = E_{\text{H}^+/\text{H}_2(\text{W})} + E_{\text{RE2(W)}} - \left(E_{\text{C}_{60}/\text{C}_{60}^{\bullet-}(\text{NB})} + E_{\text{RE1(NB)}} \right).$$

Here, $E_{\text{RE2(W)}}$ and $E_{\text{RE1(NB)}}$ are the potentials of the reference electrodes (Ag/AgCl electrodes) for the W and NB phases, respectively. Provided that

$E_{\text{RE2(W)}}$ and $E_{\text{RE1(NB)}}$ are equal,

$$\Delta E = E_{\text{H}^+/\text{H}_2(\text{W})} - E_{\text{C}_{60}/\text{C}_{60}^{\bullet-}(\text{NB})}.$$

Consequently, ΔE corresponds to the electrochemical force, E_{emf} , in eq. (2). When E_{emf} becomes negative, the H_2 evolution spontaneously proceeds according to eq. (1). If the positive current, which indicates reduction of H^+ to H_2 , is observed when ΔE is negative, the H_2 evolution is expected to spontaneously proceed. That is, it is a criterion for the spontaneous H_2 evolution that the positive final discharge appears in the negative potential region. As can be seen in the voltammograms from (iii) to (v) in Fig. 4, the positive final discharges were observed in the negative potential region at the concentration of HCl more than 5.0 M, which suggests that the H_2 evolution would proceed spontaneously when the concentration of HCl is more than at least 5.0 M.

Observation of the spontaneous H_2 evolution (Cell 2)

Based on the criterion described above, we attempted to observe the spontaneous H_2 evolution by the naked eye. We assembled a photovoltaic cell (Cell 2) shown in Fig. 2, by adding the NB solution containing 1.0 mM C_{60} , 100 mM TPATPB, and 100 mM TBPClO_4 in the

compartment for the NB phase and various strong acid solutions in the compartment for the W phase, that is, concentrated HCl (nominally 11.4 M), HClO_4 (9.2 M), and H_2SO_4 (18 M). Further, we added HClO_4 to concentrated HCl and H_2SO_4 so that the concentration of HClO_4 was 1.0 M. The reason why we added ClO_4^- in the both phases is for improving the electric conductivity. We irradiated the NB solution with the artificial solar light, as shown in Fig. 2, and took pictures of the Pt spiral electrode in the strong acid solutions (W phases) at given times and detected H_2 gas with a portable hydrogen-gas detector (TOKA SEIKI CO., LTD., Model TIP-HY) at the same time. As can be seen in Pictures (a) and (b) in Fig. 5, we found bubbles evolving around the Pt spiral electrode with the irradiation time, when concentrated HCl and HClO_4 were used, respectively. Further, we confirmed using the portable hydrogen-gas detector that the bubbles were H_2 . Obviously, no bubbles of H_2 were evolved in the absence of C_{60} , as shown in Picture (d). However, even when concentrated H_2SO_4 was used, the evolution of the bubbles of H_2 were not observed, as can be seen in Picture (c). The reason seems to be related to the activity of H^+ in the concentrated H_2SO_4 . Indeed, the spontaneous H_2 evolution was confirmed when approximately 5 M H_2SO_4 was used. Thus, the spontaneous H_2 evolution is expected to be possible by using various strong acids and their concentrations, although we did not carry out the comprehensive studies in the present work.

Finally, all chemical reactions involved in the spontaneous H_2 evolution are as follows:

For the formation of $\text{C}_{60}^{\bullet-}$,^{13), 14)}

Here, $^1\text{C}_{60}^*$ and $^3\text{C}_{60}^*$ indicate C_{60} in the singlet excited state and the triplet excited state, respectively. A neutral radical of TPB $^-$ (TPB $^{\cdot}$) is rapidly decomposed to biphenyl (Ph-Ph), (trihydroxy)phenylborate ($\text{PhB}(\text{OH})_3^-$), phenylboric acid, ($\text{PhB}(\text{OH})_2$) and so on.²⁾ Because of the rapid decomposition of TPB $^-$, the back reaction of $\text{C}_{60}^{\cdot-} + \text{TPB}^{\cdot} \rightarrow \text{C}_{60} + \text{TPB}^-$ is difficult to occur and thereby $\text{C}_{60}^{\cdot-}$ can exist with a relatively long life time in the absence of

oxidants, for example, oxygen in air. Considering that C_{60} works as a photocatalyst, the total reaction for the spontaneous H_2 evolution is expressed by

As can be seen from this chemical reaction, TPB $^-$ serves as a sacrificial reagent. Hereafter, it is necessary to develop electron donors to $^3\text{C}_{60}^*$ instead of TPB $^-$.

(a) 11.4 M HCl+1.0 M HClO₄

0 min

5 min

10 min

(c) 18 M H₂SO₄+1.0 M HClO₄

0 min

5 min

10 min

(b) 9.2 M HClO₄

0 min

5 min

10 min

(d) 11.4 M HCl+1.0 M HClO₄, no C_{60}
in the NB phase

0 min

5 min

10 min

Fig. 5. Pictures of the Pt spiral electrode in the W phases of Cell 2. The times in min denote times from the beginning of the irradiation. The W phases were 11.4 M HCl+1.0 M HClO₄ (a), 9.2 M HClO₄ (b), and 18 M H₂SO₄+1.0 M HClO₄ (c), and the NB phases contained 1.0 mM C_{60} , 100 mM TPATPB, and 100 mM TPBClO₄. For (d), the W phase was 11.4 M HCl+1.0 M HClO₄ and the NB phase did not contain C_{60} but contained 100 mM TPATPB and 100 mM TPBClO₄.

Conclusions

In order to achieve the spontaneous hydrogen (H_2) evolution by using a photochemical reaction of C_{60} , we examined voltammetric behaviors of fullerene (C_{60}) and its radical anion ($\text{C}_{60}^{\bullet-}$) using an electron conductor separating oil-water (ECSOW) system consisting of a nitrobenzene (NB) phase and a water (W) phase. From voltammetric measurements with an Au microelectrode for the NB phase and a Pt spiral electrode with a larger area than that of the microelectrode for the W phase, we observed s-shaped waves, indicating one-electron reduction of C_{60} or one-electron oxidation of $\text{C}_{60}^{\bullet-}$, which indicates that the currents are controlled by the working electrode with a much smaller area, in this case, the microelectrode. Further, analyzing the limiting currents of the s-shaped waves, we could estimate the diffusion coefficients of C_{60} and $\text{C}_{60}^{\bullet-}$ to be 3.2×10^{-6} and $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. On the other hand, we regarded an ECSOW system as a voltaic cell and considered that the potential of the voltammogram for the ECSOW system corresponds to the electromotive force for the voltaic cell. Based on this our idea, we could determine a criterion for the spontaneous H_2 evolution. In fact, based on the criterion, we successfully achieved the spontaneous H_2 evolution in the ECSOW systems consisting of a NB phase containing C_{60} and a W phase containing various concentrated acids under artificial-solar irradiation.

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