In recent years, solar cells are expected as an alternative energy since energy crisis is more serious. Substrates for solar cells have been mainly fabricated with Si crystals. However, it is important to reduce material consumption of pure Si for reductions in cost. Consequently, solar cells using compound semiconductors have been investigated because. Above all, solar cells using CdTe with II-IV type semiconductor and CuInSe2 (CIS) or Cu(In,Ga)Se2 (CIGS) with chalcopyrite-type structure have high efficiency approaching to Si solar cells and the use of In or Ga which are rare elements is expected. However, there are some problems: the use of Cd which is toxic and found out the wide stable region of Zn3P2 at lower potentials. In the cyclic voltammetry on SnO2 glass substrate, two cathodic current changes and an anodic peak were observed. This is similar results to Soliman et al., where the electrodeposition of Zn3P2 was succeeded. Consequently, the potentiostatic electrolysis thus was carried out to clarify the reduced substance and the reduction of SnO2 was only observed. When Au electrode was used as an inert electrode, the formation of Zn3P2 was not also observed, while the Au-Zn compound was confirmed. It is considered that the precipitation of zinc predominantly occurs and the reduction of phosphate ions are kinetically difficult from the results of the cyclic voltammetry. Therefore, the material without these elements is desired.

From the above background, we concentrated on Zn3P2 compound semiconductor as a solar absorber for solar cells. Zn3P2 has a direct bandgap of 1.5 eV, which is suitable for energy conversion from sunlight to electricity, and a relatively high light absorption coefficient. Therefore, Zn3P2 is a promising candidate for the material of solar cells. Wyeth and Catalano1 investigated the contact properties between Zn3P2 and various metals, and solar cells using metal/Zn3P2 schottky contact have been investigated by some researchers. Above all, the Mg/Zn3P2 solar cell shows the conversion efficiency of 6% since no data is available. The reaction for ionization of phosphoric acid, H3PO4, is expressed by

$$\text{H}_3\text{PO}_4 = \text{H}_2\text{PO}_4^- + \text{H}^+$$

The electrochemical deposition of Zn3P2 from aqueous solution containing zinc and phosphorus species has been investigated. Therefore, the electrolysis using aqueous solutions containing zinc and phosphorus species is desired. They were derived according to the method by Pourbaix.12 The thermodynamic data for the construction of potential-pH diagram are listed in Table I. Here, we defined the activity (mol/dm³) of dissolved substance M with its molar concentration [M] in molarity (mol/dm³), and the fugacity f of gaseous species g with its partial pressure p in atmosphere (atm). Since the electrolytic experiments were carried out at 363 K, the potential-pH diagram at the temperature was attempted. Unfortunately, some thermodynamic data at 363 K were not available, and we thus evaluated them by the following procedure.

For crystal species in Table I, we can obtain thermodynamic data at higher temperature from database.13 The data for aqueous species were evaluated by the following equation,

$$\Delta G_i[T] = \Delta G_i[298] - (T - 298) \Delta S_i[298],$$

where \(\Delta G_i[T]\) is the standard Gibbs energy for the formation of species i at temperature T and \(\Delta S_i[298]\) is the standard entropy for the formation of species i at 298 K. The values calculated according to the above equation are also listed in Table I. Here, the standard entropy of \(\text{H}_2\text{PO}_4^- \cdot \text{H}_2\text{O}\), \(\Delta S_i[298]\) was estimated using the data of \(\text{H}_3\text{PO}_4\) and \(\text{H}_2\text{PO}_4^-\) since no data is available. The reaction for ionization of phosphoric acid, \(\text{H}_3\text{PO}_4\), is expressed by

$$\text{H}_3\text{PO}_4 = \text{H}_2\text{PO}_4^- + \text{H}^+$$

The standard entropy change of the above reaction, \(\Delta S^e(2)\), is evaluated by the following equation.

$$\Delta S^e(2) = S^e_{\text{H}_2\text{PO}_4^-} + S^e_{\text{H}^+} - S^e_{\text{H}_3\text{PO}_4}$$

The standard entropy change at 298 K was calculated to be $-87.86$ J/mol K using the thermodynamic data in Table I.

The ionization of hypophosphoric acid, \(\text{H}_2\text{PO}_3\), and its entropy change are also expressed by

$$\text{H}_2\text{PO}_3 = \text{H}_2\text{PO}_2^- + \text{H}^+$$

and

$$\Delta S^e(4) = S^e_{\text{H}_2\text{PO}_2^-} + S^e_{\text{H}^+} - S^e_{\text{H}_2\text{PO}_3}.$$
obtained the standard Gibbs energy for the formation of $\text{H}_2\text{PO}_4^-$ at 363 K according to eq. 1. It is noted that because the extrapolated temperature range in eq. 1 is only 65 K, we do not expect any serious error associated from above assumption.

Figure 1 shows the potential-pH diagrams in acid region for Zn-H$_2$O and P-H$_2$O systems. The activity of dissolving substance was set to be 10$^{-2}$ M. In this study, red phosphorus was regarded as a standard species of phosphorus, and phosphine, PH$_3$, was not considered. The diagrams were extended to the Zn-P-H$_2$O system. First, two diagrams of the Zn-H$_2$O and P-H$_2$O systems were superimposed. The various formation reactions of Zn$_3$P$_2$ or ZnP$_2$ from zinc and phosphorus species were considered by the similar procedure as Murase et al. [10] For example, the boundary between $\text{H}_3\text{PO}_3$ + Zn$^{2+}$ and $\text{H}_2\text{PO}_3^-$ + Zn$_3$P$_2$ areas were determined by the reaction of the formation of $\text{H}_3\text{PO}_3$ and Zn$_3$P$_2$ from $\text{H}_2\text{PO}_3^-$ and Zn$^{2+}$ shown by the following equation,

$$2\text{H}_2\text{PO}_3^- + 3\text{Zn}^{2+} + 6\text{H}^+ + 8\varepsilon = \text{Zn}_3\text{P}_2 + 6\text{H}_2\text{O}. \ [6]$$

Figure 2 shows the potential-pH diagram of the Zn-P-H$_2$O system in acid region at 363 K under the activity of 10$^{-2}$ M for dissolving substance and the partial pressure of 1 atm for H$_2$ and O$_2$ gases. From the figure, one can understand that there is the stable region of Zn$_3$P$_2$ shown by shadow that suggests the electrodeposition of Zn$_3$P$_2$ is possible by the reduction of aqueous species of zinc and phosphorus. However, in this case, the competition with the generation of H$_2$ gas due to its overpotential must be considered.

**Experimental Procedure**

Aqueous solution containing sodium metaphosphate, NaPO$_3$ and zinc dichloride, ZnCl$_2$, was used as an electrolyte for electrodeposition of Zn$_3$P$_2$ according to the experiments by Soliman et al. [11] NaPO$_3$ and ZnCl$_2$ were dissolved in the deionized water with a specific resistance of larger than 5 × 10$^6$ Ωcm and their concentration is 10$^{-2}$ M. The resistivity of the solution was 5 × 10$^2$ Ωcm. The dissolution of NaPO$_3$ produces $\text{H}_3\text{PO}_4$ and/or $\text{H}_2\text{PO}_4^-$ ion in acid region. The pH of the solution was measured by pH meter and adjusted to 2.5 using $\text{H}_2\text{SO}_4$ at room temperature, 298 K, whereas electrolytic experiments were carried out at 363 K. The three-electrode cell was used for all experiments. Figure 1 shows the schematic picture for the experimental system in this study. A SnO$_2$ conductive glass substrate (ASAHI GLASS Co. Ltd., resistivity: 10 Ωcm) or Au film

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**Table 1. Thermodynamic data used in this study.** The data marked by * were calculated and that by ** was estimated in this study. See the text for details.

<table>
<thead>
<tr>
<th>Species State</th>
<th>$\Delta G_i^\circ$ [298] /kJ mol$^{-1}$</th>
<th>$S_i^\circ$ [298] /J mol$^{-1}$ K$^{-1}$</th>
<th>$\Delta G_i^\circ$ [363] /kJ mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn Crystal</td>
<td>0</td>
<td>41.63</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Zn$^{2+}$ Aqueous</td>
<td>$-147.21$</td>
<td>$-106.48$</td>
<td>$-146.08^*$</td>
<td>16</td>
</tr>
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<td>Zn$_3$P$_2$ Crystal</td>
<td>$-178.16$</td>
<td>$150.62$</td>
<td>$-174.21^*$</td>
<td>13</td>
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<tr>
<td>ZnP$_2$ Crystal</td>
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<td>$60.25$</td>
<td>$-78.37^*$</td>
<td>13</td>
</tr>
<tr>
<td>P (red) Crystal</td>
<td>$-12.028$</td>
<td>$22.85$</td>
<td>$-10.7^*$</td>
<td>13</td>
</tr>
<tr>
<td>P (white) Crystal</td>
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<td>41.07</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4$ Aqueous</td>
<td>$-1147.25$</td>
<td>$176.15$</td>
<td>$-1116.62^*$</td>
<td>16</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^-$ Aqueous</td>
<td>$-1135.12$</td>
<td>$89.12$</td>
<td>$-1098.83^*$</td>
<td>16</td>
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<td>$\text{H}_2\text{PO}_3^-$ Aqueous</td>
<td>$-856.88$</td>
<td>$167.36$</td>
<td>$-832.35^*$</td>
<td>16</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_2$ Aqueous</td>
<td>$-846.63$</td>
<td>$79.5$</td>
<td>$-816.38^*$</td>
<td>16</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_2^-$ Aqueous</td>
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<td>$158.99$</td>
<td>$-505.01^*$</td>
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<tr>
<td>$\text{H}_3\text{PO}_2$ Aqueous</td>
<td>$-512.12$</td>
<td>$71.13^{**}$</td>
<td>$-488.00^*$</td>
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<td>$\text{H}^+$ Aqueous</td>
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<td>0</td>
<td>16</td>
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<tr>
<td>$\text{H}_2\text{O}$ Liquid</td>
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<td>$69.87$</td>
<td>$-226.79^*$</td>
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<td>205.15</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Sn Crystal</td>
<td>0</td>
<td>51.195</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>SnO$_2$ Crystal</td>
<td>$-520$</td>
<td>$53.342$</td>
<td>$-506.75^*$</td>
<td>13</td>
</tr>
</tbody>
</table>

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**Figure 1.** Potential-pH diagrams of (a) the Zn-H$_2$O and (b) the P-H$_2$O systems at 363 K, where the concentration of all aqueous species is 10$^{-2}$ M.
Figure 2. Potential-pH diagram of the Zn-P-H₂O system at 363 K, where the concentration of all aqueous species is 10⁻² M. The shadow area shows the conditions to obtain Zn₃P₂.

Electrodeposited on Cu plate were used as a working electrode, and a platinum sheet (20 mm × 30 mm) was used as a counter electrode (WE and CE in Fig. 3). Au film was electrodeposited by currentstatic electrolysis with the current density of 10 mA/cm² for 300 seconds using an aqueous solution containing KAu(CN)₂ of 14 g/dm³, (NH₄)₂HPO₄ of 70 g/dm³ and K₂HPO₄ of 70 g/dm³. The temperature of the solution was 343 K. The thickness of Au film was calculated to be about 3 μm from the current density. A part of the working electrode surface was covered with substrate holder made from polypropylene so that a known area (10 × 10 mm² or 15 × 15 mm²) was exposed to the electrolyte as the surface of the working electrode. An Ag/AgCl electrode immersed in 3.3 M KCl was used as a reference electrode (RE). The electrode potentials were recalculated for standard hydrogen electrode (SHE). A glass vessel, which has the capacity of 250 cm³, was used as an electrolyte cell. The volume of the electrolytic solution was 200 cm³ and the temperature was controlled by the silicon rubber heater and the thermocouple. The actual temperature of the solution was monitored by thermometer. Cyclic voltammetry and potentiostatic electrolysis were carried out using the electrochemical analyzer (ALS, 660A). In both experiments, the solution was not stirred. The product substance after electrolysis was identified by a grazing incident X-ray diffraction (GI-XRD, PANalytical X’Pert Pro) with a copper X-ray tube and the composition was evaluated by an energy dispersive X-ray spectroscopy (EDX, EDAX VE-9800) using a scanning electron microscope (SEM, KEYENCE VE-7800). The angle of the incident beam against the surface of the sample was 1° in GI-XRD.

Experimental Results and Discussion

Re-examination of electrodeposition on SnO₂.— Figure 4 shows the cyclic voltammogram on SnO₂ conductive glass for the solution containing NaPO₃ and ZnCl₂ together with the potential-pH diagram. The potential was swept from 0 V vs. SHE to a cathodic direction and subsequently switched at −0.59 V vs. SHE. We can observe two cathodic and an anodic current changes in the figure. The current change from −0.25 vs. SHE shown by ‘a’ in Fig. 4 is due to the reduction of proton to hydrogen gas considering from the potential-pH diagram. Another cathodic reaction was observed from −0.46 V vs. SHE that is shown by ‘b’. This cathodic current change is caused from the reaction from H₂PO₄⁻ to H₂PO₃⁻, which is the reaction from a pentavalent to a tetravalent species, considering from the potential-pH diagram. The anodic current peak shown by ‘c’ was observed around at −0.23 V vs. SHE. This peak is considered to be a counter to the cathodic current change shown by ‘b’ because both current changes were monitored by thermometer. Cyclic voltammetry and potentiostatic electrolysis were carried out using the electrochemical analyzer (ALS, 660A). In both experiments, the solution was not stirred. The product substance after electrolysis was identified by a grazing incident X-ray diffraction (GI-XRD, PANalytical X’Pert Pro) with a copper X-ray tube and the composition was evaluated by an energy dispersive X-ray spectroscopy (EDX, EDAX VE-9800) using a scanning electron microscope (SEM, KEYENCE VE-7800). The angle of the incident beam against the surface of the sample was 1° in GI-XRD.

Figure 4. Cyclic voltammogram using the solution containing both ZnCl₂ and NaPO₃ and a part of potential-pH diagram of the Zn-P-H₂O system shown in Fig. 2. Solid and dotted lines in the cyclic voltammogram are the cases where the potential was switched at −0.59 V vs SHE and −0.35 V vs SHE, respectively. The arrows show the scan directions. The cathodic and the anodic currents are shown by negative and positive values, respectively.

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did not appear when the potential was reversed at switching potential of –0.35 V vs. SHE as shown in Fig. 4.

Soliman et al. also observed two cathodic current changes at –0.62 V vs. SCE and –0.75 V vs. SCE, and an anodic current peak at –0.45 V vs. SCE in the cyclic voltammetry. They used the saturated calomel electrode (SCE) as a reference. The equilibrium potential of the standard calomel electrode is about +0.24 V vs. SHE at 298 K and then we recalculated the potential for the standard hydrogen electrode in their study when we assume that the potential of the saturated calomel electrode does not change so much at 363 K; the above potentials were calculated to be –0.38 V vs. SHE, –0.51 V vs. SHE and –0.21 V vs. SHE, respectively.

Soliman et al. mentioned that the cathodic reaction at –0.38 V vs. SHE came from the reduction of expressed by the following equation,

\[ 4\text{PO}_3^- + 5e^- = \text{P} + 3\text{PO}_4^{3-}. \]  

Figure 6. EDX profiles of the SnO2 glass substrate before and after the potentiostatic electrolysis.

However, the reduction from \( \text{PO}_3^- \) to metallic phosphorus is considered to be difficult because the stability region of metallic phosphorus is at lower potential than –0.38 V vs. SHE from the potential-pH diagram. In addition, \( \text{PO}_4^{3-} \) is not stable in acid region. It is considered that this cathodic current change in their paper corresponds to the reduction of proton to hydrogen gas at –0.25 vs. SHE in this study. The second cathodic current change at –0.51 V vs. SHE was assigned to the reduction of zinc and accordingly the electrodeposition of \( \text{Zn}_3\text{P}_2 \) in the paper by Soliman et al. However, the reduction of zinc might be impossible since the equilibrium potential between Zn and \( \text{Zn}^{2+} \) is –0.83 V vs. SHE. The anodic current peak observed at –0.21 V vs. SHE is a counter to the cathodic current change at –0.51 V vs. SHE. Such a pair of current change was also observed in this study as mentioned above.

The results of the cyclic voltammetry of this study are similar to that by Soliman et al., but the interpretation is different. Consequently, the potentiostatic electrolysis was carried out at –0.59 V vs. SHE for 1 hour in order to identify the reduced substance. The reduced substance was thus identified by GI-XRD and the results were shown in Fig. 5. The diffraction pattern of metallic tin was observed together with that of \( \text{SnO}_2 \) in the X-ray diffraction profile after electrolysis. On the other hand, the peaks from \( \text{Zn}_3\text{P}_2 \) were not observed although Soliman et al. confirmed the electrodeposition of \( \text{Zn}_3\text{P}_2 \). Here, the equilibrium potential between Sn and \( \text{SnO}_2 \) is –0.32 V vs. SHE at 363 K in the case of pH = 2.5, that was calculated using the data listed in Table I. Therefore, it is likely that the reduction of \( \text{SnO}_2 \) to metallic tin occurs in the potentiostatic electrolysis and the cyclic voltammetry. Soliman et al. indentified the reduced substance as \( \text{Zn}_3\text{P}_2 \) by XRD. The peak positions of three strong lines for \( \text{Zn}_3\text{P}_2 \) and tin are listed in Table II. These positions are relatively near and it is considered that Soliman et al. might confuse the reduction of \( \text{SnO}_2 \) with the electrodeposition of \( \text{Zn}_3\text{P}_2 \). Figure 6 shows the EDX spectra before and after the electrolysis. Phosphorus was detected by EDX in the experiments where the reduction of \( \text{SnO}_2 \) was observed as shown in Fig. 6. It is considered that this comes from the adhesion of the electrolytic solution since the redox potential to obtain red phosphorus is lower than –0.59 V vs. SHE. On the other hand, the peaks of \( \text{ZnL} \) and \( \text{ZnK} \), which should appear around at 1 keV and 8.6 keV, respectively, were not detected. Consequently, it is concluded that the formation of \( \text{Zn}_3\text{P}_2 \) did not occur in this condition.

**Table II. Peak positions in XRD for \( \text{Zn}_3\text{P}_2 \) and \( \text{Sn} \).**

<table>
<thead>
<tr>
<th>Substance</th>
<th>(JCPDS card number)</th>
<th>Peak position (degree)</th>
<th>Relative intensity</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}_3\text{P}_2 )</td>
<td>(00-053-0591)</td>
<td>31.370</td>
<td>43</td>
<td>(004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.235</td>
<td>47</td>
<td>(203)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.766</td>
<td>100</td>
<td>(224)</td>
</tr>
<tr>
<td>( \text{Sn} )</td>
<td>(00-004-0673)</td>
<td>30.644</td>
<td>100</td>
<td>(200)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.018</td>
<td>90</td>
<td>(101)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.902</td>
<td>74</td>
<td>(220)</td>
</tr>
</tbody>
</table>

*Figure 5. GI-XRD profiles of the SnO2 glass substrate before and after the potentiostatic electrolysis.*
In order to investigate the electrodeposition of Zn₃P₂, the cyclic-voltammetry was carried out to the lower potentials. In this experiment, three kinds of electrolytic solution were prepared; ZnCl₂, NaPO₃, and both ZnCl₂ and NaPO₃. The concentration of each species was 0.01 M. Figure 7 shows the cyclic voltammogram where the switching potential is −1.09 V vs SHE, together with a part of potential-pH diagram of the Zn-P-H₂O system. The current change from −0.25 vs. SHE, which is observed in all solutions, is due to the reduction of proton to hydrogen gas. In the solution containing only NaPO₃, another current change is not observed and the upset of the current might come from the generation and the desorption of hydrogen gas on Au electrode. On the other hand, the cathodic current change was also observed at −0.8 V vs. SHE in the solution containing only ZnCl₂. The dashed line shows the equilibrium potential between Zn²⁺ and Zn in the potential-pH diagram. The cathodic current change was also observed at the lower potential in the solution containing both ZnCl₂ and NaPO₃. The origin of the current change is considered to be the reduction of Zn²⁺ or the formation of Zn₃P₂ considering from the potential-pH diagram and the results of other solutions. Figure 8 shows the results of EDX analysis before and after the cyclic voltammetry. The peaks related to Zn were observed in the solution containing both ZnCl₂ and NaPO₃ in addition to Au and Cu, while phosphorus was not detected. Figure 9 shows the results of GI-XRD profiles of Au electrode (a) before the voltammetry, (b) NaPO₃ solution, (c) ZnCl₂ solution and (d) solution containing both ZnCl₂ and NaPO₃ after the voltammetry. Symbols show the reference data.

Figure 7. Cyclic voltammogram on Au electrode using each solution and a part of potential-pH diagram of the Zn-P-H₂O system shown in Fig. 2. The switching potential is −1.09 V vs SHE. The dashed line shows the equilibrium potential between Zn²⁺ and Zn in the potential-pH diagram.

Figure 8. EDX profiles before and after the voltammetry when using Au electrode.

Figure 9. GI-XRD profiles of Au electrode (a) before the voltammetry, (b) NaPO₃ solution, (c) ZnCl₂ solution and (d) solution containing both ZnCl₂ and NaPO₃ after the voltammetry. Symbols show the reference data.
understood by considering the deviation from the stoichiometry. The results of XRD are consistent with those by EDX.

The formation of Zn$_3$P$_2$ was not observed on Au electrode although it was suggested in the potential-pH diagram of the Zn-P-H$_2$O system. The reduction of Zn$^{2+}$ was found in the solutions containing ZnCl$_2$, while that of phosphate ions was not observed in the solution containing only NaPO$_3$. It is assumed that the reduction of phosphate ions is kinetically difficult and the current was consumed for the reduction of zinc ions although the reduction of both ions are needed for the formation of Zn$_3$P$_2$. Therefore, the suppression of zinc precipitation might be necessary to obtain Zn$_3$P$_2$. One of considerations is the use of ligand for Zn$^{2+}$, which reduces the activity of Zn$^{2+}$.

Conclusions

In this paper, we investigated the electrodeposition of Zn$_3$P$_2$ semiconductor from aqueous solution. First, we constructed the potential-pH diagram of the Zn-P-H$_2$O system at 363 K and clarified the wide stable region of Zn$_3$P$_2$ at lower potentials. Subsequently, the cyclicvoltammetry was carried out in the same conditions as Soliman et al. and two cathodic current changes and an anodic peak were observed in the cyclicvoltamogram, where the potential was switched at −0.59 V vs. SHE. It was considered that these current changes were not related to the electrodeposition of Zn$_3$P$_2$ from the viewpoint of potential-pH diagram although Soliman et al. claimed the electrodeposition of Zn$_3$P$_2$. In the electrolysis experiment at −0.59 V vs. SHE for 1 hour, the reduction of SnO$_2$, which was used as a substrate, was observed. When Au electrode was used as an inert electrode, the formation of Zn$_3$P$_2$ was also observed although it was suggested by the potential-pH diagram. One of reasons is that the reduction of phosphate ions are kinetically difficult. In order to obtain Zn$_3$P$_2$ by electrodeposition from aqueous solutions, it is necessary that the reduction of Zn$^{2+}$ is suppressed and that of phosphate ions is enhanced.

Acknowledgments

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References