Abstract

The reaction cycles for water-splitting based on redox reactions of alkali metals are composed of four reactions, which are hydrogen generation by solid-liquid reaction, metal separation by thermolysis, oxygen generation by hydrolysis, and phase transition of the metal. Although all the cycles theoretically require more than 1000 °C in thermodynamic equilibrium condition, the reaction temperature are reduced to below 800 °C by non-equilibrium techniques using phase transition of metal vapor. In this work, thermodynamic analyses are performed by using the parameters such as operating temperature and partial pressures of the products obtained by the experiments to determine that the alkali metal redox cycles are potential hydrogen production technique as thermochemical energy storage.

1. Introduction

After fossil fuels depletion, only natural energy such as solar and wind can be utilized, and then the conversion techniques from such fluctuated energy to secondary energy are necessary as energy storage. Thus, the hydrogen production techniques are fast being studied. In the field on energy conversion of solar energy, the photovoltaic cells, photo-catalysts, and solar–heat techniques are presently developing as the power generation systems. To
utilize such methods as the hydrogen production technique, the electrolysis process should be combined. As direct hydrogen production method, a water–splitting via thermochemical reactions are also attractive. So far, the possible thermochemical water-splitting processes have been studied [1-3], and the promising processes are 2-step [4-13], I-S [14-17], and UT–3 processes [18-21]. Because the more than 800-1500 °C is necessary to generate hydrogen by using the above processes, the heat sources are limited to large-scale solar heat plants such as tower–type [21-23]. If the operating temperature of water–splitting could be lowered to below 500 °C, smaller-scale (trough-type) solar heat system can be utilized. Furthermore, thermal energy storage materials such as nitrates and carbonates can be used to stably and continuously carry out the hydrogen production without the fluctuation of solar energy [24, 25].

The water-splitting via redox reactions of alkali metals are potential cycles to operate at lower temperature than that of conventional ones. The cycles consists of following four reactions, which are (1) H₂ generation, (2) metal separation, (3) hydrolysis reactions, and (4) phase transition,

Alkali metal redox cycle 1:

\[
\begin{align*}
2\text{M OH}(s) + 2\text{M}(l) & \rightarrow 2\text{M}_2\text{O}(s) + \text{H}_2(g), \\
2\text{M}_2\text{O}(s) & \rightarrow \text{M}_2\text{O}_2(s) + 2\text{M}(g), \\
\text{M}_2\text{O}_2(s) + \text{H}_2\text{O}(l) & \rightarrow 2\text{M OH}(s) + 1/2\text{O}_2(g), \\
\text{M}(g) & \rightarrow \text{M}(l). 
\end{align*}
\]

M are alkali metals, lithium Li, sodium Na, and potassium K. In our previous work, it is indicated that the Li and Na cycles are operated below 800 and 500 °C, respectively, under non-equilibrium conditions [26, 27].

In this work, the possibility of the alkali metal redox cycles are discussed by thermodynamic analyses based on database and the parameters such as operating temperature and partial pressure of the gaseous products obtained by the experiments.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
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<tbody>
<tr>
<td>(\Delta G^0)</td>
<td>Gibbs free energy change</td>
</tr>
<tr>
<td>(\Delta H^0)</td>
<td>standard enthalpy change</td>
</tr>
<tr>
<td>(T)</td>
<td>temperature</td>
</tr>
<tr>
<td>(\Delta S)</td>
<td>entropy change</td>
</tr>
<tr>
<td>(\Delta S^0)</td>
<td>standard entropy change</td>
</tr>
<tr>
<td>(R)</td>
<td>gas constant</td>
</tr>
<tr>
<td>(p_0)</td>
<td>standard pressure (constant)</td>
</tr>
<tr>
<td>(p_{\text{pco}})</td>
<td>partial pressure of the gaseous product</td>
</tr>
<tr>
<td>(\Delta H_{\text{H}_2\text{O}})</td>
<td>enthalpy change of H₂O decomposition</td>
</tr>
<tr>
<td>(Q_{\text{input}})</td>
<td>input energy required to operate endothermic reactions in the cycles</td>
</tr>
<tr>
<td>(\delta)</td>
<td>ratio of heat recovery</td>
</tr>
<tr>
<td>(Q_{\text{exo}})</td>
<td>energy generated by exothermic reactions in the cycles</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>effective absorptance for solar radiation</td>
</tr>
<tr>
<td>(I)</td>
<td>intensity of solar radiation</td>
</tr>
<tr>
<td>(C)</td>
<td>concentration ratio of the solar concentrating system</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>emittance of the receiver</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>(T_L)</td>
<td>temperature of low temperature part</td>
</tr>
</tbody>
</table>
2. Thermodynamic analyses

The alkali metal cycles were discussed by the following thermodynamic analyses. The thermodynamic properties such as operating temperature of each endothermic reaction were calculated by using the Gibbs free energy change $\Delta G$ as follows,

$$\Delta G = \Delta H^0 - T \Delta S,$$

$$\Delta S = \Delta S^0 + R \ln \left( \frac{p_0}{p_{\text{pro}}} \right),$$

where the $\Delta H^0$ and $\Delta S^0$ were calculated by the database [28] and the temperature dependence was ignored in the analyses.

The efficiency of the water-splitting cycle is defined by the following equation,

$$\eta_{\text{cycle}} = \frac{\Delta H_{\text{H}_2O}}{Q_{\text{input}} - dQ_{\text{exo}}},$$

Furthermore, the efficiency of the solar heat systems as heat sources for water-splitting is expressed by efficiency of solar absorption and Carnot cycle as follows [3],

$$\eta_{\text{system}} = \eta_{\text{absorption}} * \eta_{\text{carnot}} = \frac{\alpha_s IC - \alpha e T^4}{IC} * \frac{T - T_0}{T},$$

where it is assumed that $T_L = 20$ °C, $I = 1$ kW / m$^2$, and $\alpha_s = e = 1$ for the analyses in this work.

3. Results and discussion

The $\Delta H^0$, $\Delta S^0$, and operating temperatures $T_{\text{exp}}$ of each reaction on the alkali metal cycles for the generation of 1 mol H$_2$ are shown in Table 1. The details of experiments to obtain $T_{\text{exp}}$ are shown in our previous works [26, 27]. In the experiments, the non-equilibrium techniques were adapted for the endothermic reactions to realize the low-temperature water-splitting. In addition, the $\Delta H^0$ and $\Delta S^0$ for the decomposition of peroxide M$_2$O$_2$ is also shown as R(M$_2$O$_2$) in Table 1 because it is experimentally indicated that M$_2$O$_2$ is decomposed in the case of Li cycle. Considering the decomposition of M$_2$O$_2$ to M and O$_2$, the reaction cycles are modified as follows,

Alkali metal redox cycle 2:

$$\begin{align*}
2\text{MOH(s)} + 2\text{M(l)} & \rightarrow 2\text{M}_2\text{O(s)} + \text{H}_2\text{(g)}, \\
2\text{M}_2\text{O(s)} & \rightarrow 2\text{M}_2\text{O}_2\text{(s)} + 2\text{M(g)}, \\
\text{M}_2\text{O}_2\text{(s)} & \rightarrow 2\text{M(g)} + \text{O}_2\text{(g)}, \\
2\text{M(l)} + 2\text{H}_2\text{O(l)} & \rightarrow 2\text{MOH(s)} + \text{H}_2\text{(g)}, \\
4\text{M(g)} & \rightarrow 4\text{M(l)}. 
\end{align*}$$

On the basis of the parameters in Table 1, the thermodynamic analyses were performed..

<table>
<thead>
<tr>
<th>Li cycle</th>
<th>Na cycle</th>
<th>K cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0$</td>
<td>$\Delta S^0$</td>
<td>$T_{\text{exp}}$</td>
</tr>
<tr>
<td>R(1)</td>
<td>-232</td>
<td>53</td>
</tr>
<tr>
<td>R(2)</td>
<td>883</td>
<td>258</td>
</tr>
<tr>
<td>R(3)</td>
<td>-51</td>
<td>62</td>
</tr>
<tr>
<td>R(4)</td>
<td>-314</td>
<td>-210</td>
</tr>
<tr>
<td>R(M$_2$O$_2$)</td>
<td>951</td>
<td>426</td>
</tr>
</tbody>
</table>
3.1. Li cycle

As shown in Table 1, the reactions except for metal separation are exothermic. In fact, the reaction (1) and (3) were easily completed below 500 °C. The metal separation is endothermic reaction with large $\Delta H^0$, 883 kJ/mol. Experimentally, 800 °C was required even under the non-equilibrium condition to generate Li. In addition, the experimental results suggested that Li$_2$O$_2$ was decomposed at such high temperature. Fig. 1 shows Gibbs free energy change of reaction (2) and Li$_2$O$_2$ decomposition. When the partial pressure of Li(g) is 0.1 MPa under equilibrium condition, more than 3000 °C is necessary. On the other hand, the reaction temperature is decreased to 800 °C under non-equilibrium condition produced by the solidification of Li vapor. In this case, the partial pressure of Li vapor is estimated to be about 1×10$^{-29}$ Pa, which is very low and might be realized by the solidification. The temperature dependence of $\Delta G$ was changed by using the above partial pressure obtained from the experiment to thick line in Fig. 1. Assuming that the pressure of gaseous products of Li(g) and O$_2$(g) generated by Li$_2$O$_2$ decomposition could be decreased to be the same value as the reaction (2), the $\Delta G$ can be calculated. As a result, it is found that the Li$_2$O$_2$ decomposition proceeds easier than the reaction (2), suggesting that the Li$_2$O$_2$ generated by the metal separation is immediately decomposed. The analytic results are consistent with the experimental results. Thus, the Li cycle is classified into the cycle 2.

![Fig. 1. Thermodynamic analyses on Gibbs free energy change of the metal separation (2) for the Li cycle.](image)

3.2. Na cycle

The H$_2$ generation reaction (1) of the Na cycle is small endothermic reaction. $\Delta G^0 < 0$ is easily satisfied even in equilibrium condition as shown in Fig. 2(a). In fact, it was experimentally clarified that the reaction proceeded at 350 °C. The operating temperature of metal separation (2) was 500 °C in the experiments, and then the partial pressure of Na vapor was estimated to be about 1×10$^{-19}$ Pa. Fig. 2(b) shows the results of thermodynamic analyses for the metal separation (2) and peroxide decomposition. By using the partial pressures of gaseous products obtained by the experiment, the temperature dependence of $\Delta G$ on the metal separation is changed from thin to thick line. Na$_2$O$_2$ is not decomposed at 500 °C even under low partial pressure, which is feasible to operate the reaction (2). This analytic result suggests that the metal separation is prior reaction to the Na$_2$O$_2$ decomposition at 500 °C. In fact, the Na$_2$O$_2$ formation was indicated in the experiments at 500 °C. The hydrolysis (3) of the Na cycle was easily completed by the heating up to 100 °C. Therefore, the Na cycle is categorized into the cycle 1 and is operated at lower operating temperature than the Li cycle.
For the K cycle, the $\Delta H^\circ$ of the H$_2$ generation is larger than those of other cycles, suggesting that the partial pressure of H$_2$ has to be decreased to operate the reaction below 500 °C. In our experiments, the catalyzed Mg was used to absorb H$_2$ generated the reaction (1) and reduce the partial pressure. Fig. 3(a) shows $\Delta G$ for the reaction (1) and the H$_2$ sorption of Mg at 500 °C as a function of partial pressure of H$_2$. The lower partial pressure than $1 \times 10^{-2}$ Pa is necessary for the reaction progress. The equilibrium pressure of Mg at room temperature 25 °C is about $5 \times 10^{-2}$ Pa, which is slightly higher than the required low-pressure. Thus, it is expected that the Mg as H$_2$ absorbent should be placed at below 20 °C for the progress of the reaction (1) at 500 °C. The $\Delta G$ for H$_2$ absorption of Mg shown in Fig. 3(a) is obtained with $T = 5$ °C. In this case, the non-equilibrium condition can be realized, and the H$_2$ release of the reaction (1) would proceed. Although Mg is used to reduce the partial pressure of H$_2$ in our experiments, the more efficient technique is required to realize the low partial pressure for the practical use. The metal separation (2) of K cycle has the lowest $\Delta H^\circ$ value among the other cycles. Assuming that the partial pressure could be reduced to be same level as the Na cycle by using our experimental systems, the operating temperature is speculated to be about 400 °C as shown in Fig. 3(b).
Here, the reaction (1) needs at least 500 °C as mentioned above, thus the reaction (2) would immediately proceed after the reaction (1). The speculation is consistent with the thermodynamic analyses shown in Fig. 3(b). These results indicate that the reaction (1) and (2) continuously proceed, and then K would act as pseudo catalyst. The K₂O₂ decomposition required higher temperature than the reaction (2) even under low partial pressures, suggesting that the K cycle is classified to the cycle 1.

3.4. Efficiency and feasibility

Assuming that the water-splitting is operated by the cycle 1, theoretical efficiency $\eta_{\text{cycle}}$ of the Li, Na, and K cycles are calculated to be 32, 52, and 54% without heat recovery of exothermic reactions ($Q_{\text{exo}} = 0$), respectively. These values are lower than that of IS process, 67%. To obtain the comparable efficiency to the IS process, the alkali metal cycles requires the heat recovery of at least 50%. Here, the products of each reaction of the alkali metal cycles are one solid and one gas phase. When the each reaction is completed step by step, it is not necessary to transfer the solid product during the cycle, and the only transfer system of gaseous phases is required. In other words, the reaction system is simply constructed with membrane and solidification system of the metal vapor, indicating that the high heat recovery ratio $\delta$ due to the easy handling of materials is expected. Thus, the cycle 1 would be recognized as a feasible technique. Moreover, under the operation procedure proposed above, the gaseous phases such as H₂ and metal vapor are removed and completely separated from the reaction field, suggesting that the side reaction such as metal and H₂O can be prevented.

On the other hand, in the case of cycle 2, the materials transfers are more difficult from the cycles 1. In the decomposition process of M₂O₂ (11), the gaseous products M(g) and O₂(g) should be separated simultaneously without the reaction to form M₂O₂ again. Moreover, the generated 4M should be divided to half amounts for the two kinds of H₂ generation process, (9) and (12). Consequently, the cycle 2 has poor feasibility due to the difficult and complicated material transfers, suggesting that the Li cycle categorized in the cycle 2 is difficult to be used as practical application.

Fig. 4 shows schematic image of the alkali metal cycles categorized as type 1. To increase the efficiency, the heat recovery of phase transition is important issue. As mentioned above, the cycle is ideally operated by only one reactor, and the solidification of metal vapor at isolated part is essentially necessary to realize water-splitting at low temperature. Therefore, it is expected that the heat generated from the phase transition can be efficiently recovered by using above reaction system.

If the alkali metal cycles are used as conversion technique of solar heat, the efficiency is decreased depending on the efficiency of solar heat systems $\eta_{\text{system}}$. Fig. 5 shows $\eta_{\text{system}}$ with C=100 and 5000, which are concentration ratios of typical trough and beam-down types [3]. By using the low concentration system at 500 °C, the efficiency is decreased to about 25%. The efficiency at 500 °C reaches to 60% in the case of the high concentration system. Here, if the heat recovery is realized, the efficiency can be enhanced. From the point of view for the efficiency, the alkali metal cycles operated at low-temperature is worse than the conventional water-splitting operated at high temperature about 1000 °C because the efficiency is essentially limited by the Carnot efficiency $\eta_{\text{carnot}}$. However, the alkali metal cycles has an advantage on real efficiency, which includes the time dependence with fluctuation of solar energy. The operating temperature of Na and K cycles are suitable for utilization of heat storage materials such as nitrates and carbonates, suggesting that the cycles are possibly operated for longer time than that of high temperature types by establishing the efficient operating system.
Fig. 4. Schematic image of the alkali metal cycles.

Fig. 5. Theoretical efficiency of the solar heat systems with $C = 100$ (trough type) and 5000 (beam-down type).

4. Conclusion

In this work, the alkali metal cycles were analyzed by the thermodynamic point of view by using the previous experimental data. The analytic results were consistent with the experimental results. The Li cycle requires 800 °C to operate all the reactions and is classified to the cycle 2 including the peroxide decomposition, which is complicated and difficult to be operated. The Na system was suitable to be utilized below 500 °C because of the moderate thermodynamic properties to independently operate the composed reactions. The K cycle is also potential water-splitting system at 500 °C. Furthermore, it is expected that the reaction (1) and (2) continuously proceed. In this case, the cycle is simpler than the cycle 1.

From the point of view on the efficiency, the heat recovery has to be necessary to obtain the high efficiency for the conversion of solar heat. Because of the low operating temperature of the Na and K cycles, the heat storage materials can be utilized efficiently. Thus, it is expected as advantage of the cycles that the H$_2$ is able to be produced in longer time than the conventional thermochemical water-splitting.

References