Hydrogen Production via Thermochemical Water Splitting Process by Alkali Metal Redox Cycle

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In this review, the reaction cycles based on redox reactions of alkali metals such as lithium, sodium, and potassium are systematically investigated as a potential water splitting technology operated at lower temperature than 500 °C. Assuming that all the cycles are operated in thermodynamic equilibrium condition, more than 1000 °C is theoretically required. Thus, equilibrium shift using phase transition of alkali metals is performed to decrease the reaction temperatures. The operating temperature of the lithium cycle is 800 °C because such high temperature is necessary to obtain high vapor pressure. The potassium cycle is potentially water splitting operated below 500 °C. However, strong corrosion is serious problem to develop it as practical application. Among them, the sodium cycle reveals the lowest operating temperature, which is 400 °C. Therefore, the sodium cycle should be categorized as one of the potential water splitting technology.

Key Words
Hydrogen production, Water splitting, Thermochemical cycle, Alkali metal, Equilibrium shift

1. Introduction

After fossil fuels depletion, only renewable energy such as solar and wind can be utilized, and then the conversion technology from such fluctuated energy to secondary energy is necessary. The electricity is useful secondary energy and its technologies and infrastructure for utilization have already been established. However, the energy density of batteries as electricity storage is not sufficiently high, thus it is not suitable for long distance transportation and a large amount of energy storage with a demand of our life. Hydrogen is also one of attractive secondary energy because of its high gravimetric energy density compared with the batteries, suggesting that it can be used as media for storage and transportation of the large amount of energy. Recently, the hydrogen production, storage, and utilization technologies are fast being studied. As the current hydrogen production methods, the steam reforming methods are attractive and efficient. However, the resources are basically fossil fuels such as hydrocarbons, indicating that this technology is unable to use after the depletion of fossil fuels. Ideally, hydrogen should be produced from the renewable energy. The water electrolysis by using hydro and wind power generation is regard as representative hydrogen production method and its technology has almost been established. For solar energy, the utilization of photovoltaic cell, solar-heat generator, and photocatalysts are presently developing as

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the power generation systems. To utilize such methods as the hydrogen production technology, the electrolysis system should be combined. As direct hydrogen production systems, a water splitting via thermochemical cycles\(^\text{11–13}\) are also attractive because a high efficiency can be expected in principle. In addition, the thermochemical cycles have advantages for the scaled up as a chemical plant for mass production. While the area of electrodes should be extended into 2 dimensional planes for scale up of the electrolysis systems, hydrogen can be produced via chemical reactions in 3 dimensional reactors for the thermochemical cycles. So far, the potential thermochemical water splitting processes have been sorted by using thermodynamic databases because they are composed of several step chemical reactions. The promising thermochemical cycles such as 2-step\(^\text{8–10}\), Iodine-Sulfur (I-S)\(^\text{14–17}\), and UT-S\(^\text{18–20}\) requires more than 800 °C for the operation. For utilization of the conventional thermochemical cycles, large scale solar-heat generators (tower type), which can generate higher temperature than 1000 °C due to the high concentration of solar right, is required\(^\text{22–23}\). If the water splitting could be operated below 600 °C, smaller scale solar-heat generators (tough type) and unused energy resources such as exhaust heat from any factories are available. Furthermore, efficient heat storage materials such as nitrates and carbonates can be used for the continuous hydrogen production even at night\(^\text{24–25}\). As low-temperature water splitting technology, the following reaction systems by water splitting via redox reactions of alkali metals are proposed\(^\text{26–29}\):\[
\begin{align*}
2\text{MOH(s)} + 2\text{M(l)} & \rightarrow 2\text{MO(s)} + \text{H}_2(g), \quad (1) \\
2\text{M}(s) & \rightarrow \text{M}_2\text{O}_2(s) + 1/2\text{O}_2(g), \quad (2) \\
\text{M}_2\text{O}_2(s) + \text{H}_2\text{O}(l) & \rightarrow 2\text{MOH}(s) + \text{H}_2(g), \quad (3) \\
\text{M}(g) & \rightarrow \text{M}(s) \rightarrow \text{M}(l), \quad (4)
\end{align*}
\]
where, M is alkali metals such as lithium Li, sodium Na, and potassium K. This system is composed of (1) H₂ generation, (2) metal separation, (3) hydrolysis reactions, and (4) phase transition. The standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\) of each reaction for all the systems were calculated by database\(^\text{30–31}\) and shown in Table 1, where \(\Delta H^0\) and \(\Delta S^0\) are estimated for the generation of 1 mol of H₂. Among them, the K-cycle was reported in the patent assigned by Gaz de France\(^\text{32}\) and literatures\(^\text{33–35}\), the Na-cycle was also described without experimental data as a series of the K-cycle to utilize the high temperature heat energy (more than 1000 °C) obtained from nuclear reactor. In 2012, we demonstrated that the Na-cycle is possibly operated below 500 °C by controlling the thermodynamic equilibrium conditions\(^\text{36}\).

In this review, we have focused on the water splitting by the alkali metal redox reaction as the thermochemical cycle. The feasible conditions of each reaction are separately investigated, where equilibrium shift by decreasing partial pressure of gaseous products to enhance the entropy was adopted for the endothermic reactions. From the results of systematic experiments, the difference of the properties between cycles as water splitting is discussed. In addition, the efficiency of the cycles is theoretically analyzed, and the reaction system to efficiently operate the alkali metal redox cycles are proposed.

### 2. Equilibrium shift by decreasing partial pressure

The reactions in the alkali metal redox cycles are performed at fixed pressure and temperature conditions, and thus the thermodynamics of a chemical reaction is expressed by the following Gibbs free energy change \(\Delta G\).

\[
\Delta G = \Delta H - T \Delta S,
\]

where \(\Delta H\) is enthalpy change, \(T\) is reaction temperature, \(\Delta S\) is entropy change, \(S\) is entropy, \(R\) is the gas constant, \(p_i\) is the standard pressure (constant), and \(p_{\text{pro}}\) is the partial pressure of the gaseous product. The second term of equation (6) is contribution of partial pressure when the gaseous materials are included in reactions. Since \(\Delta H\) is determined by the difference between thermodynamic stability of starting materials and products in chemical reactions, the reaction temperature \(T\) to satisfy \(\Delta G < 0\) is lowered with larger \(\Delta S\). Namely, entropy term is changed by controlling the partial pressure of the product \(p_{\text{pro}}\), and then the equilibrium condition of the reaction is changed. By continuously removing the gaseous product from the reaction field, the reaction could be completed at lower temperature. In the alkali metal redox cycles,

| H₂ generation | Metal separation | O₂ generation | Phase transition |
|---------------|-----------------|---------------|-----------------|
| ΔH⁰ | ΔS⁰ | ΔH⁰ | ΔS⁰ | T eq | ΔH⁰ | ΔS⁰ | ΔH⁰ | ΔS⁰ |
| Li | -232 | 53 | 883 | 258 | 3200 | -51 | 62 | -314 | -210 |
| Na | 11 | 36 | 540 | 252 | 1900 | -55 | 66 | -210 | -192 |
| K | 119 | 18 | 409 | 246 | 1400 | -68 | 77 | -173 | -178 |
the metal separation reaction (2) is most difficult reaction thermodynamically. However, the entropy term can be increased by reducing the partial pressure of metal vapor because the above alkali metals melt with generation of vapor pressure below 500 °C. Thus, the equilibrium shift is useful to control the reaction temperature.

The feasible reaction conditions are separately discussed for each reaction as fundamental research although all the reactions in the cycle should be continuously operated for the practical application. The reaction (1) was performed by using home-made apparatus as shown in Fig. 1(a). To qualitatively and quantitatively analyze the generated H₂, magnesium Mg catalyzed by niobium(V) oxide Nb₂O₅, which is denoted as c-Mg, was used. c-Mg was installed at separate part connected to the reaction field, suggesting that only generated H₂ is able to reach there. It was reported by Hanada et al. and can absorb H₂ even at room temperature33,34, then the equilibrium pressure of H₂ is 4 × 10⁻² Pa (ΔH° = 76 kJ/mol H₂, ΔS° = 133 J/mol H₂ K, T = 25 °C), which is almost vacuum condition. Namely, the partial pressure of generated H₂ decreases due to the absorption by c-Mg.

For the metal separation reaction (2), the reactor has been designed and assembled to control the equilibrium conditions. It is equipped with the cooling part as shown in Fig. 1(b) to separate the metal vapor from the reaction field by condensation of metals. For the generation reactions of gases such as H₂ and O₂, additional energy is required to decrease partial pressure to enhance entropy change of the reaction and recover the ambient pressure (condensation) besides the energy to control chemical reaction. On the other hand, in the alkali metal cycles, phase transitions of metals are utilized to decrease the partial pressure of gaseous alkali metals, and the energy to enhance the entropy and condensation is included in the cycles as reaction (4). Here, the details of sample and experiments are described in supporting information.

3. Hydrogen production properties

3.1 Li-cycle

The H₂ generation reaction (1) of the Li-cycle is exothermic reaction as shown in Table 1, suggesting that this reaction proceeds even in a closed system. The Li metal granule and LiOH powder with Li molar ratio was heated by using the reactor shown in Fig. 1(a). Fig. 2(a) shows the results of X-ray diffraction (XRD) measurement (Cu Kα radiation) for the reaction products obtained after the heat treatments at 300, 400, and 500 °C. After the reaction at 300 °C, diffraction peaks were mostly corresponding to LiOH of the starting material. A diffraction peak assigned to Li₂O was observed at 2θ = 34° as shown by allow although its intensity is very weak. To estimate the amount of generated H₂ due to the reaction between Li and LiOH, the hydrogen desorption properties of c-Mg used as H₂ absorbent in the experimental system was examined. As a result, the H₂ desorption from c-Mg was clearly observed as shown in Fig. 2(b). Here, the H₂ desorption profile with two peaks is caused by the state of catalyzed c-Mg, and we discuss only whether H₂ is ab/desorbed or not because the H₂ desorption profile is not important in this experiment. The molar ratio of c-Mg used as the H₂ absorbent was chosen to be c-Mg/M (in reaction (1)) = 1. Thus, half of c-Mg is hydrogenated when the reaction proceeds completely, then its hydrogen capacity is 3.5 mass% (full capacity is about 7.0 mass%). Thus, the reaction yield can be estimated by analyzing the amount of H₂ absorbed in c-Mg. The mass spectroscopy (MS) result suggested that H₂ was desorbed from 300 °C although the reaction yield was only 20%, which was estimated by the weight loss (about 0.7 mass%) obtained by thermogravimetry (TG). The Li₂O phase obviously grew and the yield of H₂ generation was enhanced to be about 30% with increasing temperature to 400 °C. However, the starting materials remained. After the reaction at 500 °C, Li and LiOH phases disappeared and the observed peaks were totally assigned to Li₂O, indicating that the reaction was completed. The drastic enhancement of reaction yield would be caused by the different reaction processes due to the temperature region. At 300 °C, the reaction proceeded by the solid-liquid (LiOH(s)-Li(l)) reaction. In this case, when LiOH was formed on surface of LiOH(s), the continuous reaction might be suppressed or slowed by the oxide layers. Here, it is expected that LiOH decomposition would affect the reaction processes at high temperature region. The thermal decomposition properties of LiOH itself was investigated, and the result is shown in Fig. 2(c). The H₂O desorption was clearly observed from 350 °C, suggesting that LiOH decomposed and desorbed H₂O to form Li₂O under He flow condition. Thus, the reaction process was
Fig. 2  (a) XRD patterns of starting materials and products at 300, 400, and 500 °C (references: Li PDF #15-0401, Li2O PDF #73-0593, and LiOH PDF #76-0911), (b) TG-MS profiles of c-Mg as absorbent of H2. (c) TG-MS profiles of LiOH.

essentially changed at higher temperature region as follows,

\[ 4\text{LiOH(s)} \rightarrow 2\text{Li}_2\text{O(s)} + 2\text{H}_2\text{O(g)}, \]  

(7) 

\[ 2\text{Li(l)} + 2\text{H}_2\text{O(g)} \rightarrow 2\text{LiOH(s)} + \text{H}_2(g). \]  

(8)

The reaction between molten Li(l) and generated \( \text{H}_2\text{O(g)} \) is easily proceed compared with the above solid-liquid reaction process. Via the continuous cycle reactions expressed by eq. (7) and (8), the starting materials were totally changed to \( \text{Li}_2\text{O} \) and \( \text{H}_2 \). At 400 °C, the decomposition rate of LiOH would be slow in the closed experimental system. In fact, c-Mg desorbed only \( \text{H}_2 \) in the case of the reaction at 400 °C. On the other hand, large amount of \( \text{H}_2\text{O} \) was released from c-Mg used for the reaction at 500 °C, indicating that part of \( \text{H}_2\text{O} \) generated by LiOH decomposition reacted with c-Mg to form Mg(OH)\(_2\).
The metal separation expressed as equation (2) is endothermic reaction. For this reaction, about 3400 °C is required under equilibrium condition at \( p_{Li} = 0.1 \) MPa. The reaction temperature is possibly lowered by reducing the partial pressure of gaseous Li, which can be realized by condensation of Li as solid phase because vapor pressure of solid should be almost zero. For preparing above reaction conditions, the experimental system was specially designed and assembled as shown in Fig. 1 (b). Li2O was heated in the reactor, and the products at the cooling (upper) and heating (bottom) parts were analyzed. Although no product was found at the cooling part in the case of reaction at 500 °C, a little amount of solid product was deposited at cooling part after the reaction at 800 °C. The product was analyzed by inductively coupled plasma-atomic emission spectroscopy, where the obtained products were solved into the water for the elemental analysis, because the identification by XRD measurement was difficult. As a result, the luminescence peaks originated in Li element were clearly observed at 671.8 and 61.4 nm, which were typical luminescence from Li element. Above results suggest that the Li atoms are included in the deposited product. Li and Li2O were expected as the materials included in the deposited product because the melting point of these materials was lower than the experimental temperature. To accurately identify the products, optimization of reaction conditions to obtain larger amount of products and further analyses are required. The XRD patterns of the starting material and the product at the bottom part of the reactor after the reaction at 800 °C are shown in Fig. 3 (a). The XRD pattern was mainly corresponding to that of Li2O phase, and the peaks assigned to Li2O2 were not observed. On the other hand, the integrated peak intensity of Li2O was slightly decreased after the reaction, suggesting that a little amount of Li2O was consumed by the reaction. To further determine the generation of Li and Li2O, the product at 800 °C reacted with H2O at 300 °C. The hydrolysis reactions of alkali metals and their compounds were expected as follows,

\[
\text{M}_2\text{O}(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{MOH}(s), \quad (9)
\]

\[
\text{M}(l) + \text{H}_2\text{O}(l) \rightarrow \text{MOH}(s) + \frac{1}{2}\text{H}_2(g). \quad (10)
\]

If Li and Li2O were formed, H2 and O2 should be generated by the reaction (9) and (3), respectively. Fig. 3 (b) shows the results of gas chromatography (GC) for inside gas in the reactor after the hydrolysis of products. The generation of H2 was clearly revealed, suggesting that Li would be formed by the metal separation reaction and some amount of Li remained at the bottom part due to the low evaporation rate at the temperature. However, significant O2 generation was not observed, where the observed peak corresponding to O2 is very weak as same as that of background. This result indicated that no Li2O2 was formed although Li was generated. The inconsistent results would be caused by the thermal stability of Li2O. Tanifuji et al. reported that Li2O is decomposed into Li2O and O2 under Ar atmosphere at higher temperature than 300 °C, suggesting that Li2O2 would be immediately decomposed after generation by the metal separation (2) at more than 500 °C. The decomposition of Li2O easily proceeds in the thermodynamic calculation.
using data base (See Fig. S2). Thus, the products at bottom part were Li₂O and Li, indicating that only H₂ should be generated by the hydrolysis. From above results, it is speculated that the metal separation proceeds at 800 °C although the modification and optimization of reaction conditions are required. In addition, the high reaction temperature and low reaction yield were also problems. It is thought that these problems are caused by low vapor pressure of Li at around 500 °C, in other words, more than 800 °C is required to generate sufficient amount of Li vapor even though the reaction entropy could be controlled. Thus, the further improvement of thermodynamic and kinetic properties is necessary to realize the reaction progress at lower temperature.

The hydrolysis reaction (3) is exothermic. In the experiment, the reaction between high purity Li₂O₂ and excess molar amount of liquid H₂O (not ideal molar ratio 1:1) was carried out at 200 and 300 °C. Fig. 4 (a) shows the XRD patterns of the starting material Li₂O₂ and the products. The commercial Li₂O₂ contained a small amount of LiOH as an impurity. After the hydrolysis reaction at 200 °C, the intensity of diffraction peaks corresponding to Li₂O₂ was decreased, however it remained. It was confirmed that Li₂O₂ was completely changed to LiOH at 300 °C. These results indicate that 300 °C is necessary to realize the fast diffusion of H₂O molecule in LiOH(s), which is formed on Li₂O₂(s) surface at an initial stage of the hydrolysis reaction. In addition, it was clearly clarified by GC that the gaseous product at 300 °C was only O₂ as shown in Fig. 4 (b). As discussed above, the O₂ generation should be originated in the hydrolysis of peroxide because the reaction of LiOH as small amount of impurity with H₂O generates no gases. These results indicate that 300 °C is sufficient for completing the hydrolysis reaction.

3.2 Na-cycle

For the H₂ generation reaction (1), since the enthalpy change of the reaction is not large. The equilibrium temperature to generate 0.1 MPa of H₂ is about 35 °C. The Na metal and NaOH powder with 1:1 molar ratio was put into the reactor and heated. Fig. 5 (a) shows the XRD pattern of the product formed by the reaction (1) at 300 and 350 °C. After the reaction at both temperatures, the new peaks were observed and were assigned to Na₂O and NaH. The diffraction peaks corresponding to the starting materials of NaOH and Na were still observed even at 350 °C, suggesting that the reaction was not completed. The formation of Na₂O indicates the progress of the expected reaction. The NaH phase was byproduct in the experimental conditions, which would be formed by the reaction between the remaining Na and the generated H₂ during the cooling process after the heat treatment. NaH would not be generated when the reaction proceeds completely because NaH decomposes to Na and H₂ above 300 °C. Here, the experiment at 500 °C was also performed to realize higher reaction yield. However, the expected results were not able to be obtained because it was found that Na was evaporated and moved out from reaction field. The TG-MS results for c-Mg used as the H₂ absorbent are shown in Fig. 5 (b). The
H₂ desorption was clearly observed in the MS spectrum, indicating that H₂ was generated by the reaction between NaOH and Na above 300 °C. The weight loss by the H₂ desorption of c-Mg used as the H₂ trap for the reactions at 300 and 350 °C was about 0.4 and 2.8 mass%, and then the reaction yields can be estimated to be 10 and 80%, respectively, because the ideal hydrogen absorption amount in c-Mg with the molar ratio Na:Mg = 11 is 3.5 mass% assuming 100% of yield for the reaction described by eq. (1). Regarding the practical use, the reaction yield should be reached to 100%. Therefore, the reaction kinetics should be improved by using catalysts and/or scaffolds.

The metal separation expressed as equation (2) is the most difficult reaction thermodynamically, where about 2000 °C is required in thermodynamic calculation under equilibrium condition at p_{H₂} = 0.1 MPa. However, the reaction temperature can be lowered by reducing the Na vapor pressure down to quite low pressure like the Li-cycle. The XRD patterns of the as-synthesized Na₂O, the product at the upper (cooling) part, and the product at the bottom part of the reactor after the reactions at 400 and 500 °C are shown in Fig. 6 (a). From the XRD pattern of the as-synthesized Na₂O, it was confirmed that the main phase was Na₂O, although a small amount of NaOH was included as an impurity. After the reaction at 400 °C, a metallic and ductile material was found at the cooling part (See photos in Fig. S3 (a)). Although the observed peak in the XRD measurements at 400 °C are weak intensity due to the small amount of the collected product, this peak was assigned to main diffraction peak of Na metal phase. The above results indicated that the metal separation reaction proceeded even at 400 °C. Here, the small peaks observed at 500 °C except for those of Na might be corresponding to NaOH and/or oxides as impurity, which would be generated by the reaction between small parts of Na and air during the sample transfer and measurement of XRD. At 500 °C, the amount of condensed Na was significantly larger and the diffraction peak intensity of the Na₂O phase was lowered. In the XRD pattern of the product at the bottom part, the peaks with high intensity corresponded to Na₂O and NaOH, although Na₂O₂ was the expected product of reaction (2). It was difficult to assign the other weak peaks such as 34 and 36° even though the position of some peaks might be close to those of Na₂O₂. The results suggest that unexpected reactions such as a reaction between the Na₂O₂ phase and the reactor might occur on a small scale to form unidentified phases. Here, the corrosion at 400 °C would be relatively weaker than that at 500 °C because the unidentified peaks observed at 400 °C were smaller and weaker. As the reasons that Na₂O₂ was not observed in XRD measurement, it was considered that the generated Na₂O₂ was amorphous or decomposed to Na₂O and O₂ at 500 °C like the Li-cycle (37) – (40). To confirm the formation of Na₂O₂, the product of reaction (2) was reacted with H₂O, and then the generated gases were analyzed by GC. The three types of hydrolysis reactions, which are eq. (3), (9), and (10), for the Na and Na-related compounds are expected...
as mentioned in the discussion of the Li-cycle. Thus, when Na2O2 exists in the product, O2 should be generated by the reaction with H2O. The results of GC as shown in Fig. 6 (b) revealed the presence of O2 and H2, suggesting that Na2O2 and Na existed in the products generated by the metal separation reaction. The reaction yield was roughly estimated by comparing the ratios of integrated peak intensity for Na2O obtained before and after the reaction at 400 and 500 °C, and the result was about 35 and 80%, respectively. From the results, the possibility that reaction (2) proceeds below 500 °C under the low partial pressure of Na was demonstrated. However, considering practical use, the reaction kinetics should be improved to complete the reaction and the corrosion effect should be minimized by further investigation such as development of materials for the reactor.

The reaction between Na2O2 and H2O of excess molar ratio was carried out at 100 °C. Fig. 7 (a) shows the XRD patterns of the as-synthesized Na2O2 and the product by the reaction with H2O. As shown in the upper XRD pattern, the as-synthesized Na2O2 contained a small amount of NaOH as an impurity. After the hydrolysis reaction, it was confirmed that Na2O2 was completely changed to NaOH hydrate, indicating that the hydrolysis reaction proceeded. The NaOH hydrate was formed by a reaction between NaOH generated by reaction (3) and the remaining H2O. To identify the gaseous product, GC was performed for the gas inside the reactor after the reaction. The result is shown in Fig. 7 (b). It was clearly clarified that the gaseous product was mainly O2 with small amount of H2, where the small amount of H2 would be caused by the impurity Na in the synthesized Na2O2 (See experimental details in supporting information). This result indicates that 100 °C is sufficient for completing the hydrolysis reaction. Here, when the H2O(l) was put into the reactor at room temperature, temperature increase of several °C was detected by the reaction with Na2O2. Thus, the hydrolysis is potentially operated without heating.

### 3.3 K-cycle

The H2 generation reaction (1) of the K-cycle is endothermic reaction with larger ΔH and smaller ΔS0 than those of other cycles as shown in Table 1. In the thermodynamic calculation, it is expected that more than 500 °C is necessary even under low H2 partial pressure, which is equilibrium pressure about 10^-2 Pa of c-Mg as the H2 absorbent at 25 °C.28 The reaction was carried out by using K and KOH with 1:1 molar ratio at 500 °C for 20 h. The XRD patterns of the product are shown in Fig. 8 (a) with the results of starting materials, and TG-MS results of c-Mg are shown in Fig. 8 (b). Although the peaks corresponding to K and KOH disappeared, no K2O phase as expected product was found. The assignment of new peaks observed after the reaction were difficult because of the low intensity and complicated patterns. It was speculated that this phase was formed due to the strong corrosion of the K-related materials at 500 °C. In fact, the sample
collection after the reaction was quite difficult although the powder samples were obtained in the case of Li and Na cycles. This phenomenon is also an evidence of corrosion. Regarding the corrosive effects, the details are discussed later. H₂ was desorbed from c-Mg used as absorbent, and then the weight loss was 0.8 mass% for 3.5 mass% as the maximum capacity in this experimental system. By using the TG result, the reaction yield was roughly estimated to be about 20%. Here, at 300 °C, no obvious reaction was clarified because the remaining KOH were found in the XRD measurement. These results roughly corresponded to the thermodynamic speculation.

For the metal separation (2), the K₂O, which is synthesized from K and O₂ with 4:1 molar ratio by heating up to 100 °C, was heat-treated at 400 and 500 °C for 10 h. Fig. 9 shows the XRD patterns of as-synthesized K₂O and products at the cooling part and at bottom part of the reactor shown in Fig. 1 (b). Even at 400 °C, significant amount of material with metallic color and typical ductile
Fig. 9 XRD patterns of K$_2$O and products condensed at the cooling part and at bottom part of the reactor at 400 and 500 °C (reference: K$_2$O$_2$ PDF #32-0827, KOH, K, K$_9$Ni$_2$O$_7$ (PDF #71-1987), and K$_2$O)

properties of alkali metals was found at the cooling part (See Fig. S3 (b)). The product was identified as K, indicating that the metal vapor was generated during the reaction. At bottom part, the K$_2$O phase totally disappeared and the product was not able to be assigned by the same problems as the case of H$_2$ generation reaction. After the reaction 500 °C, larger amount of K was generated at cooling part, and then the unexpected diffraction peaks were observed. These peaks were assigned to ternary oxides K$_9$Ni$_2$O$_7$, suggesting that the materials containing K reacted with the reactor made from Ni based alloys above 400 °C. In addition, we have tested the reaction at 500 °C by using the Au coated reactor to prevent the corrosion. However, Au-K alloys were formed, indicating that the corrosion of K-related materials is quite strong (See Fig. S4). Here, the H$_2$ generation reaction required at least 500 °C as mentioned above, and the metal separation proceeded at 400 °C. If the reaction between K and KOH is performed at 500 °C, the reaction (1) and (2) could proceed continuously as follows,

$$2\text{KOH}(l) + 2\text{K}(l) \rightarrow \text{K}_2\text{O}_2(s) + 2\text{K}(g) + \text{H}_2(g).$$  
(11)

In this case, the separation of H$_2$ and K vapor is difficult, leading to the low reaction yield. Moreover, in ICSC card, it is reported that K$_2$O is melted and decomposed at 350 °C. Therefore, it is expected that the reaction at 500 °C proceeds via complicated processes considering above facts. To understand the essential reaction process of the K-cycle, the corrosion as the most serious problem should be prevented.

Fig. 10 (a) and (b) shows the XRD and GC results for the solid and gaseous products obtained by the hydrolysis reaction at 200 °C for K$_2$O$_2$ and excess molar amount of H$_2$O. Here, potassium peroxide K$_2$O$_2$ was synthesized by a reaction between K$_2$O and O$_2$ with 2:1 molar ratio at room temperature. The as-synthesized K$_2$O$_2$ was completely changed to KOH hydrate, and then O$_2$ was generated with
Table 2 Reaction yield of each reaction and corrosion on the alkali metal cycles

|          | H₂ generation | Metal separation | O₂ generation |
|----------|---------------|------------------|---------------|
|          | Temp. (°C)    | Yield (%)        | Temp. (°C)    | Yield (%)        | Temp. (°C)    | Yield (%)  | corrosion |
| Li       |               |                  |               |                  |               |            |           |
| 300      | 10            | 500              | -             | 200              | -             | undetectable |
| 400      | 25            | 800              | little        | 500              | 10            |            |
| 500      | 100           | -                | -             | -                | -             | -           |
| Na       |               |                  |               |                  |               |            |           |
| 300      | 10            | 400              | 35°           | RT               | -             | detectable |
| 350      | 80            | 500              | 80°           | 100              | 100           |            |
| K        |               |                  |               |                  |               |            |           |
| 300      | -             | 400              | -             | 200              | 100           | strong     |
| 500      | 20°           | 500              | -             | -                | -             | -           |

*rough estimation without contribution of corrosion.

small amount of H₂ originated in impurity K inside of K₂O₂. These results suggest that the hydrolysis reaction almost completely proceed at the conditions.

The operating temperature of the alkali metal cycles are summarized in Table 2 together with the reaction yield by rough estimation and the degree of corrosion. By using the equilibrium shift, the operating temperatures of all the cycles are reduced. For the Li-cycle, the H₂ and O₂ generation are completed below 500 °C, and the corrosion was not clearly found even at high temperature. However, the metal separation reaction has problems, which are requirement of high temperature 800 °C, the decomposition of Li₂O₂, and the low reaction yield. The Na-cycle can be operated at the lowest operating temperature, 400 °C, among the cycles. Furthermore, the total reaction yield is experimentally 60% under the reaction conditions without contribution of the corrosion and kinetics. The K-cycle is also potential system to be operated below 500 °C. However, the strong corrosion is serious problem to effectively and safely control the cycle for practical use.

4. Potential efficiency and operation system

The theoretical efficiency of the thermochemical water splitting process is defined as follows,

\[
\eta_{\text{cycle}} = \frac{\Delta H_{\text{H₂O}}}{(Q_{\text{in}} - \delta Q_{\text{exo}})} \quad (12)
\]

where, \(\Delta H_{\text{H₂O}}\) is enthalpy change of H₂O decomposition under standard condition (286 kJ / mol) and \(Q_{\text{in}}\) is input energy required to operate endothermic reactions in the cycles, which is supplied from heat source. \(\delta\) and \(Q_{\text{exo}}\) are a ratio of heat recovery and energy generated by exothermic reactions in the cycles, respectively. Here, for further practical situations, some working energy are required to operate the reaction processes. For instance, the hydrogen generation reaction of the K system should be operated under low partial pressure of H₂ due to thermodynamic reason as described above although the Na system proceeds without the pressure control. Namely, the extra energy is required to pressure reduction and condensation of H₂ in the K system. For the metal generation processes, the entropy should be increased by reducing partial pressure of gaseous alkali metals. However, the partial pressure of metals decreases by condensation as liquid or solid phase at cooling part. Since phase transition of metals is included as one of reactions in the cycles, the additional energy to control vapor pressure is not necessary. The efficiency variation as a function of the heat recovery ratio \(\delta\) are shown in Fig. 11 together with that of the IS process as reference. The IS process is studying as potential hydrogen production cycle at present and is operated around 800 °C, which is lower temperature than that required for the cycles of high temperature type such as 2-step cycles. The x-axis is the recovery ratio of heat by exothermic reactions including the cycles. The IS process has the high theoretical efficiency about 67 % even without any heat recovery. The efficiency of Na- and K-cycle is about 50 %, and the Li-cycle has the lowest efficiency of them because only the metal separation is endothermic. 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, assuming that the complete reactions could be realized. In this case, it is not necessary to transfer the solid phase in the cycle, and only the systems for H₂ separation and the condensation of metal vapor are required. In other words, the reaction system is simply constructed with membrane and collection part of metal, indicating that the high heat recovery ratio $\delta$ and low working energy $W$ due to the easy handling of materials are expected. This is also recognized as the advantage point of the alkali metal cycles for practical use compared with the water splitting systems including difficult material handling such as solid-solid and liquid-liquid separations. Considering the peroxides decomposition discussed above, the reaction (2) and (3) in the cycles are modified as follows \(^{(13)}\),

\[
2\text{M}_2\text{O}(s) \rightarrow 4\text{M}(g) + \text{O}_2(g), \quad (13)
\]

\[
2\text{M}(l) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{MOH}(s) + \text{H}_2(g). \quad (14)
\]

Fig. 12 Reaction scheme with heat transfer and image of potential reaction process for the Na-cycle
In this case, 4 moles of M generated by reaction (13) should be divided into half amount and transferred into the reaction (I) and (14), suggesting that the reaction handling should be complicated.

Fig. 12 shows scheme of the Na-cycle, which possesses the best performance among the alkali metal cycles because of the low operating temperature, weak corrosion, and abundant resource. As mentioned above, the reactions (1-3) shown by solid thick frames in Fig. 12 are ideally operated in the same reactor without the transfer of solid products. In this case, the handling system of Na vapor shown by broken frame in Fig. 12 is important because the recovery of large exothermic heat by the phase transition process, which is totally -210 kJ, is essential to obtain the higher efficiency. If 60 % of heat generated in this process could be recovered, the system efficiency ηecon reaches about 70 %, which is comparable with the IS process. In addition, the value of W is possibly reduced by the simple reaction system as well. For the development as practical application, the moderate reaction speed to operate the cycle is necessary. However, the contribution is not included in the efficiency discussed above. Thus, the factors related to time based on the kinetics of the cycles should be investigated as next research step.

5. Conclusions

In this review, the feasible reaction conditions of the water splitting by the alkali metal redox cycles were systematically investigated. To operate the cycles at lower temperature, the equilibrium shift by decreasing partial pressure of gaseous products was adapted for the endothermic reactions. The alkali metal cycles consist of four processes, which are the H₂ generation (I); 2MOH+2M → 2M+M+H₂, the metal separation (2); 2M+O → M₂O₂+2M, and hydrolysis (3); M₂O₂+H₂O → 2MOH+1/2O₂, and the phase transition of alkali metal (4); 2M(g) → 2M(l). The operating temperature of the Li-cycle was 800 °C due to large endothermic of the metal separation reaction although the reaction (I) and (3) was almost completed below 500 °C. It was demonstrated that the Na-cycle was possibly operated below 400 °C even though the improvement of kinetics and suppression of corrosion were issues to obtain high efficiency for the energy conversion. It was difficult to operate the K-cycle by thermodynamic and corrosive reasons, particularly the development of the reactor materials to prevent the corrosion should be required. Therefore, the Na-cycle is suitable to be utilized as practical application due to the lower operating temperature than 500 °C. Although the theoretical efficiency of the Na-cycle is only about 50 %, it is expected that the efficiency can be enhanced to 70 % by the recovery of heat generated in the phase transition (4), which would be realizable target by establishing the simple reaction system.

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Supporting information

1. Experimental details

1.1 Sample preparation

Commercial Li (99.9+%, Aldrich), Na (99.9%, Aldrich), K (99.95%, Aldrich), lithium hydroxide LiOH (99.99%, Aldrich), sodium hydroxide NaOH (99.998%, Aldrich), potassium hydroxide KOH (>99%, Aldrich), lithium oxide Li2O (>99%, Kojundo Chemical Laboratory), and lithium peroxide Li2O2 (>99%, Kojundo Chemical Laboratory) were used as the starting materials, where KOH was purified by heat treatment at 250 °C to dehydrate because commercial one included considerable amount of KOH hydrate. Sodium oxide Na2O was synthesized by the heat treatment at 300 °C under dynamic vacuum condition for 20 h of NaH (95%, Aldrich) and NaOH mixture, which was prepared by ball-milling (P7, Fritsch) under 1 MPa of H2 for 2 h. Potassium oxide K2O was synthesized by heating K and O2 with 4:1 molar ratio to 100 °C. Sodium peroxide Na2O2 and potassium peroxide K2O2 were synthesized by a reaction of Na2O and K2O with O2 by 2:1 molar ratio at 300 °C and room temperature, respectively.

1.2 Experimental procedure and analyses

The feasible reaction conditions are separately investigated for each reaction as fundamental research...
although the reactions included in the cycle should be continuously operated. The reaction (1) was performed with 1:1 molar ratio of M:MOH in the temperature range from 300 to 500 °C under Ar atmosphere for 20 h in a closed system by using home-made apparatus as shown in Fig. 1 (a). To qualitatively and quantitatively analyze the generated H₂, magnesium Mg catalyzed by niobium(V) oxide Nb₂O₅, which is denoted as c-Mg, was used. c-Mg was installed at separate part connected by the stainless-steel tube to the reaction field of M and MOH, suggesting that only generated H₂ is able to reach there. It was reported by Hanada et al. and can absorb H₂ even at room temperature (ΔH₀ = 76 kJ/mol H₂, ΔS₀ = 133 J/mol H₂ K, T = 25 °C), which is almost vacuum condition. c-Mg was synthesized by the same procedure as that reported in the literature. The molar ratio of c-Mg used as the H₂ absorbent was chosen to be c-Mg/M=1. Thus, half of c-Mg is hydrogenated when the reaction (1) proceeds completely, then its hydrogen capacity is 3.5 mass% (full capacity is about 7.0 mass%). Thus, the reaction yield can be estimated by analyzing the amount of hydrogen absorbed in c-Mg. For the metal separation reaction (2), the reactor has been designed and assembled to control the equilibrium shift. It is equipped with the cooling part as shown in Fig. 1 (b) to separate the metal vapor from gaseous products generated by the solidification of Li vapor. In this case, the partial pressure of Li is theoretically about 1 × 10⁻²⁹ Pa, which is very low and might be realized by the solidification. The temperature dependence of ΔG was changed by using the above Li partial pressure obtained from the experiment at 800 °C as thick line. Assuming that the pressure of gaseous products generated by Li₂O decomposition can be decreased to be the same value as the reaction (2) in the same experimental system, the temperature dependence of ΔG is obtained.

Fig. S2 Thermodynamic analyses on Gibbs free energy change of reaction (2) and Li₂O₂ decomposition. If the partial pressure of Li(g) is 0.1 MPa under equilibrium condition, extreme high temperature of more than 3000 °C is necessary. On the other hand, the reaction temperature is decreased to 800 °C under low pressure of metal vapor produced by the solidification of Li vapor. In this case, the partial pressure of Li is theoretically about 1 × 10⁻²⁹ Pa, which is very low and might be realized by the solidification. The temperature dependence of ΔG was changed by using the above Li partial pressure obtained from the experiment at 800 °C as thick line. Assuming that the pressure of gaseous products generated by Li₂O₂ decomposition can be decreased to be the same value as the reaction (2) in the same experimental system, the temperature dependence of ΔG is obtained.

Fig. S3 Photos of products condensed at the cooling part and at bottom part of the reactor for (a) Na- and (b) K-cycle. The spring shape wire in the photos is part of cooling system. The condensed materials have metallic shining and ductile feature, which are typical properties of alkali metals. In fact, the XRD pattern of the products shows diffraction peaks corresponding to each metal phases.

Fig. S4 XRD patterns of K₂O and products at bottom part of the Au-coated reactor for the metal separation reaction of the K-cycle at 500 °C. The XRD patterns of Au5K (PDF# 50-1039), Au1.7K (PDF# 39-9094), KOH (PDF #78-0190), K₂O (PDF #65-2992), and K₂O₂ (PDF #32-0827) were referred from a database.
the reaction field by condensation of solid metals. The heat
treatment of M₂O was carried out in the temperature range
from 400 to 800 °C for 10 or 20 h under vacuum condition
in a closed system. To investigate the hydrolysis reaction (3),
M₂O₂ was heated in the temperature range from 100 to 300
°C together with excess molar amount of liquid H₂O under
0.1 MPa of Ar in a closed system. All the samples were
handled in a glove box (MP-P60W, Miwa MFG) filled with
purified Ar gas (>99.999%) to avoid the influence of air.
The reaction expecting strong corrosion was performed in
the reactor made from Ni-based alloy (Inconel®) (Umetoku
Co. Ltd.).

The solid materials before and after each reaction
were identified by X-ray diffraction XRD measurement
(RINT-2100, Cu Kα radiation, Rigaku), where all the samples
were covered by a polyimide sheet (Kapton®, Du Pont-
Toray) in the glove box to avoid the influence of air during
the measurement, and inductively coupled plasma-atomic
emission spectroscopy ICP-AES (ICPE-9000, Shimadzu),
where water is used as a solvent. The analyses of the
luminescence spectra were performed by using a database
in software (ICPESolution, Shimazu). To quantitatively
evaluate the H₂ generated by reaction (1), the c-Mg was
analyzed by a thermal desorption mass spectroscopy MS
(M-QA200TS, Anelva) connected to thermogravimetry
TG (TG8120, Rigaku). In this thermal analysis, high purity
helium (He) gas (>99.9999%) was flowed as a carrier gas
and the heating rate was fixed at 5 °C/min. The gaseous
products were analyzed by gas chromatography GC (GC-14B,
Shimadzu). In the case of hydrolysis reaction, the reactor
was soaked into iced water to freeze the remaining H₂O. In
the GC measurement, the temperature of the column was
set to be 100 °C, and high purity Ar gas was flowed as a
carrier gas.

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