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Thermochemical energy storage by water-splitting via redox reaction of alkali metals

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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.

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1. Introduction

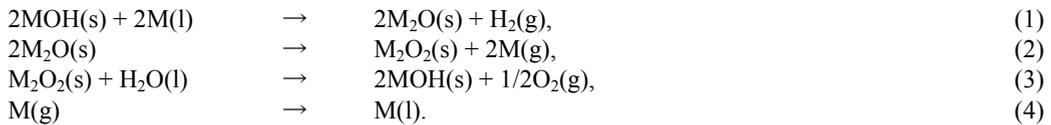
After fossil fuels depletion, only natural energy such as solar and wind can be utilized, and then the conversion techniques from such fluctuated energy to secondary energy are necessary as energy storage. Thus, the hydrogen production techniques are fast being studied. In the field on energy conversion of solar energy, the photovoltaic cells, photo-catalysts, and solar-heat techniques are presently developing as the power generation systems. To

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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:



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.

Nomenclature

ΔG^0	Gibbs free energy change
ΔH^0	standard enthalpy change
T	temperature
ΔS	entropy change
ΔS^0	standard entropy change
R	gas constant
p_0	standard pressure (constant)
p_{pro}	partial pressure of the gaseous product
$\Delta H_{\text{H}_2\text{O}}$	enthalpy change of H ₂ O decomposition
Q_{input}	input energy required to operate endothermic reactions in the cycles
δ	ratio of heat recovery
Q_{exo}	energy generated by exothermic reactions in the cycles
α_s	effective absorptance for solar radiation
I	intensity of solar radiation
C	concentration ratio of the solar concentrating system
ε	emittance of the receiver
σ	Stefan-Boltzmann constant
T_L	temperature of low temperature part

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 ΔG as follows,

$$\Delta G = \Delta H^0 - T\Delta S, \quad (5)$$

$$\Delta S = \Delta S^0 + R \ln \left(\frac{p_0}{p_{pro}} \right), \quad (6)$$

where the ΔH^0 and ΔS^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,

$$\eta_{\text{cycle}} = \frac{\Delta H_{\text{H}_2\text{O}}}{Q_{\text{input}} - \delta Q_{\text{exo}}}, \quad (7)$$

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],

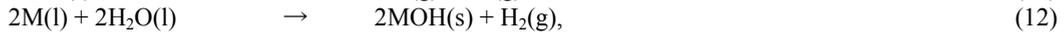
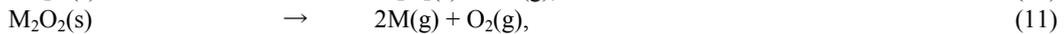
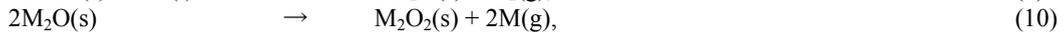
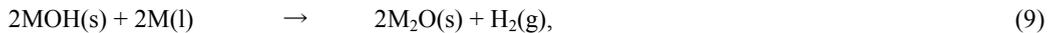
$$\eta_{\text{system}} = \eta_{\text{absorption}} * \eta_{\text{carnot}} = \frac{\alpha_s IC - \varepsilon T^4}{IC} * \frac{T - T_L}{T}, \quad (8)$$

where it is assumed that $T_L = 20$ °C, $I = 1$ kW / m², and $\alpha_s = \varepsilon = 1$ for the analyses in this work.

3. Results and discussion

The ΔH^0 , ΔS^0 , and operating temperatures T_{exp} of each reaction on the alkali metal cycles for the generation of 1 mol H₂ are shown in Table 1. The details of experiments to obtain T_{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 ΔH^0 and ΔS^0 for the decomposition of peroxide M₂O₂ is also shown as R(M₂O₂) in Table 1 because it is experimentally indicated that M₂O₂ is decomposed in the case of Li cycle. Considering the decomposition of M₂O₂ to M and O₂, the reaction cycles are modified as follows,

Alkali metal redox cycle 2:



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

Table 1. Enthalpy change ΔH^0 (kJ/mol), entropy change ΔS^0 (J/mol K), and operating temperatures T_{exp} (°C) obtained by the experiments of each reaction on the alkali metal cycles for the generation of 1 mol H₂. In addition, ΔH^0 and ΔS^0 of decomposition of 1 mol M₂O₂ are also shown.

	Li cycle			Na cycle			K cycle	
	ΔH^0	ΔS^0	T_{exp}	ΔH^0	ΔS^0	T_{exp}	ΔH^0	ΔS^0
R(1)	-232	53	500	11	36	350	119	18
R(2)	883	258	800	540	252	500	409	246
R(3)	-51	62	300	-55	66	100	-68	77
R(4)	-314	-210	-	-210	-192	-	-173	-178
R(M ₂ O ₂)	951	426	-	726	418	-	674	413

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 ΔH^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_2O_2 was decomposed at such high temperature. Fig. 1 shows Gibbs free energy change of reaction (2) and Li_2O_2 decomposition. When the partial pressure of $\text{Li}(\text{g})$ 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 ΔG 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 $\text{Li}(\text{g})$ and $\text{O}_2(\text{g})$ generated by Li_2O_2 decomposition could be decreased to be the same value as the reaction (2), the ΔG can be calculated. As a result, it is found that the Li_2O_2 decomposition proceeds easier than the reaction (2), suggesting that the Li_2O_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.

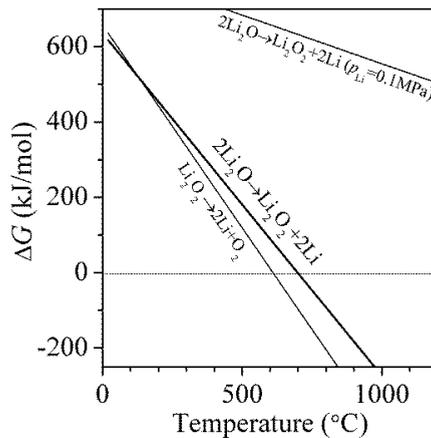


Fig. 1. Thermodynamic analyses on Gibbs free energy change of the metal separation (2) for the Li cycle.

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 ΔG on the metal separation is changed from thin to thick line. Na_2O_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_2O_2 decomposition at 500 °C. In fact, the Na_2O_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.

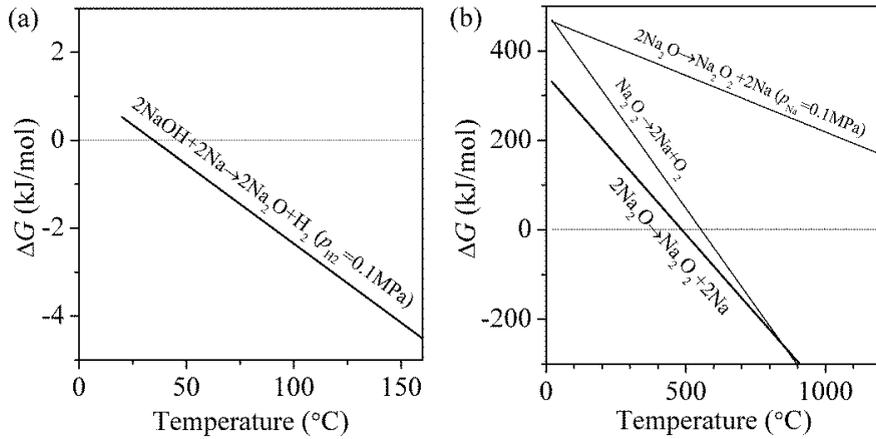


Fig. 2. Thermodynamic analyses on Gibbs free energy change of (a) the H₂ generation (1) and (b) metal separation (2) for the Na cycle.

3.3. K cycle

For the K cycle, the ΔH^0 of the H₂ generation is larger than those of other cycles, suggesting that the partial pressure of H₂ has to be decreased to operate the reaction below 500 °C. In our experiments, the catalyzed Mg was used to absorb H₂ generated the reaction (1) and reduce the partial pressure. Fig. 3(a) shows ΔG for the reaction (1) and the H₂ sorption of Mg at 500 °C as a function of partial pressure of H₂. The lower partial pressure than 1×10^{-2} Pa is necessary for the reaction progress. The equilibrium pressure of Mg at room temperature 25 °C is about 5×10^{-2} Pa, which is slightly higher than the required low-pressure. Thus, it is expected that the Mg as H₂ absorbent should be placed at below 20 °C for the progress of the reaction (1) at 500 °C. The ΔG for H₂ 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 H₂ release of the reaction (1) would proceed. Although Mg is used to reduce the partial pressure of H₂ 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 ΔH^0 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).

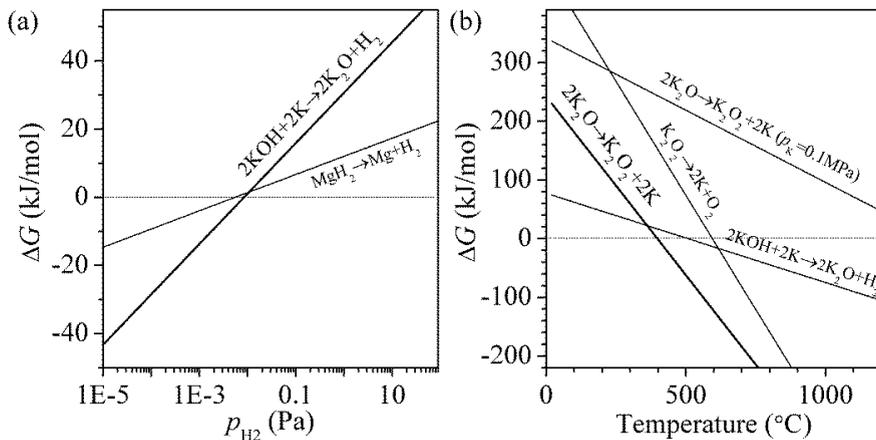


Fig. 3. Thermodynamic analyses on Gibbs free energy change of (a) the H₂ generation (1) and (b) metal separation (2) for the K cycle.

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 K_2O_2 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 η_{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 δ 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 H_2 and metal vapor are removed and completely separated from the reaction field, suggesting that the side reaction such as metal and H_2O 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 M_2O_2 (11), the gaseous products $M(g)$ and $O_2(g)$ should be separated simultaneously without the reaction to form M_2O_2 again. Moreover, the generated 4M should be divided to half amounts for the two kinds of H_2 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 η_{system} . Fig. 5 shows η_{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 η_{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.

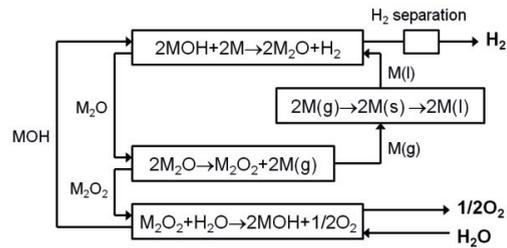
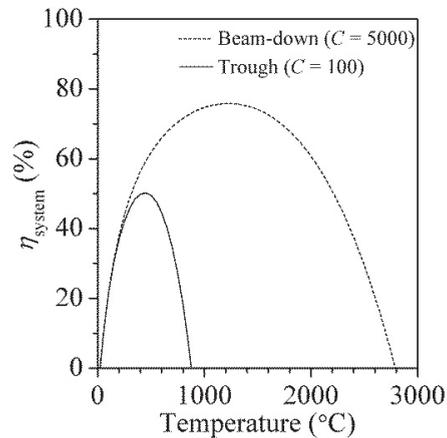


Fig. 4. Schematic image of the alkali metal cycles.

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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ because of the moderate thermodynamic properties to independently operate the composed reactions. The K cycle is also potential water-splitting system at 500 $^{\circ}\text{C}$. 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

- [1] Yalçın S. A review of nuclear hydrogen production. *Int. J. Hydrogen Energy* 1989;14:551-61.
- [2] Abanades S, Charvin P, Flamant G, Neveu P. Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy. *Energy* 2006;31:2805-22.
- [3] Kodama T, Gokon N. Thermochemical Cycles for High-Temperature Solar Hydrogen Production. *Chem. Rev.* 2007;107:4048-77.
- [4] Nakamura T. Hydrogen production from water utilizing solar heat at high temperatures. *Solar Energy* 1977;19:467-75.

- [5] Ambriz JJ, Ducarroir M, Sibieude F. Preparation of cadmium by thermal dissociation of cadmium oxide using solar energy. *Int. J. Hydrogen Energy* 1982;7:143-53.
- [6] Sibieude F, Ducarroir M, Tofighi A, Ambriz J. High temperature experiments with a solar furnace: The decomposition of Fe_3O_4 , Mn_3O_4 , CdO . *Int. J. Hydrogen Energy* 1982;7:79-88.
- [7] Steinfeld A, Sanders S, Palumbo R. Design aspects of solar thermochemical engineering- case study: Two-step water-splitting cycle using the $\text{Fe}_3\text{O}_4/\text{FeO}$ redox system. *Solar Energy* 1999;65:43-53.
- [8] Ehrensberger K, Frei A, Kuhn P, Oswald HR, Hug P. Comparative experimental investigations of the water-splitting reaction with iron oxide Fe_{1-y}O and iron manganese oxides $(\text{Fe}_{1-y}\text{Mn}_y)_{1-y}\text{O}$. *Solid State Ionics* 1995;78:151-60.
- [9] Kodama T, Kondoh Y, Yamamoto R, Andou H, Satou N. Thermochemical hydrogen production by a redox system of ZrO_2 -supported Co(II) -ferrite. *Solar Energy* 2005;78:623-31.
- [10] Weidenkaff A, Steinfeld A, Wokaun A, Auer PO, Eichler B, Reller A. Direct solar thermal dissociation of zinc oxide: condensation and crystallisation of zinc in the presence of oxygen. *Solar Energy* 1999;65:59-69.
- [11] Lundberg M. Model calculations on some feasible two-step water splitting processes. *Int. J. Hydrogen Energy* 1993;18:369-76.
- [12] Gokon N, Hasegawa T, Takahashi S, Kodama T. Thermochemical two-step water-splitting for hydrogen production using Fe-YSZ particles and a ceramic foam device. *Energy* 2008;33:1407-16.
- [13] Gokon N, Murayama H, Nagasaki A, Kodama T. Thermochemical two-step water splitting cycles by monoclinic ZrO_2 -supported NiFe_2O_4 and Fe_3O_4 powders and ceramic foam devices. *Solar Energy* 2009;83:527-37.
- [14] O'Keefe D, Allen C, Besenbruch G, Brown L, Norman J, Sharp R, McCorkle K. Preliminary results from bench-scale testing of a sulfur-iodine thermochemical water-splitting cycle. *Int. J. Hydrogen Energy* 1982;7:381-92.
- [15] Kubo S, Nakajima H, Kasahara S, Higashi S, Masaki T, Abe H, Onuki K. A demonstration study on a closed-cycle hydrogen production by the thermochemical water-splitting iodine-sulfur process. *Nucl. Eng. Des.* 2004;233:347-54.
- [16] Sakurai M, Nakajima H, Amir R, Onuki K, Shimizu S. Experimental study on side-reaction occurrence condition in the iodine-sulfur thermochemical hydrogen production process. *Int. J. Hydrogen Energy* 2000;25:613-19.
- [17] Takai T, Kubo S, Nakagiri T, Inagaki Y. Lab-scale water-splitting hydrogen production test of modified hybrid sulfur process working at around 550 °C. *Int. J. Hydrogen Energy* 2011;36:4689-701.
- [18] Kameyama H, Tomino Y, Sato T, Amir R, Orihara A, Aihara M, Yoshida K. Process simulation of "Mascot" plant using the UT-3 thermochemical cycle for hydrogen production. *Int. J. Hydrogen Energy* 1989;14:323-30.
- [19] Kameyama H, Yoshida K. Reactor design for the UT-3 thermochemical hydrogen production process. *Int. J. Hydrogen Energy* 1981;6:567-75.
- [20] Sakurai M, Bilgen E, Tsutsumi A, Yoshida K. Adiabatic UT-3 thermochemical process for hydrogen production. *Int. J. Hydrogen Energy* 1996;21:865-70.
- [21] Sakurai M, Bilgen E, Tsutsumi A, Yoshida K. Solar UT-3 thermochemical cycle for hydrogen production. *Solar Energy* 1996;57:51-58.
- [22] Roeb M, Säck JP, Rietbrock P, Prah C, Schreiber H, Neises M, de Oliveira L, Graf D, Ebert M, Reinalter W, Meyer-Grünefeldt M, Sattler C, Lopez A, Vidal A, Elsberg A, Stobbe P, Jones D, Steele A, Lorentzou S, Pagkoura C, Zygogianni A, Agrafiotis C, Konstandopoulos AG. Test operation of a 100kW pilot plant for solar hydrogen production from water on a solar tower. *Solar Energy* 2011;85:634-44.
- [23] Säck JP, Roeb M, Sattler C, Pitz-Paal R, Heinzel A. Development of a system model for a hydrogen production process on a solar tower. *Solar Energy* 2011;86:99-111.
- [24] Dincer I, Dost S. A perspective on thermal energy storage systems for solar energy applications. *International Journal of Energy Research* 1996;20:547-57.
- [25] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, Cabeza LF. State of the art on high temperature thermal energy storage for power generation. Part 1- Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews* 2010;14:31-55.
- [26] Miyaoka H, Ichikawa T, Nakamura N, Kojima Y. Low-temperature water-splitting by sodium redox reaction. *Int. J. Hydrogen Energy* 2012;37:17709-14.
- [27] Nakamura N, Miyaoka H, Ichikawa T, Kojima Y. Hydrogen production via thermochemical water-splitting by lithium redox reaction. *J. Alloys Compd. in press.*
- [28] National Institute of Standards and Technology, *NIST Chemistry WebBook*, <http://webbook.nist.gov/chemistry/>.