*Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 329–336*

# THERMODYNAMICS AND KINETICS OF STEAM SPLITTING OVER A POTASSIUM ALUMINOSILICATE ELECTROLYTE[*]

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## Abstract

A novel system using a potassium aluminosilicate electrolyte under applied potential that is able to split $H_2O$ (or $OH^-$) into $H_2$ and $1/2O_2$ (or $O_2^{2-}$) with higher yields than the value deduced from Faraday's law is presented. There were three steps by which $H_2$ and $O_2$ were generated stoichiometrically, and it was predicted that the high yields were due to the occurrence of chemically endothermic reactions: dehydration of the catalytic cell at a temperature below 100°C (step I), disproportionation of KOH ($2KOH \rightarrow H_2+K_2O_2$) at a temperature around 200°C (step II), and disproportionation of $K_2O$ ($2K_2O \rightarrow K_2+K_2O_2$) at a temperature above 500°C (step III). So-called Nemca might be caused in the course of step III, since the rate of $H_2$ was ca $10^2$ times larger than the value deduced from Faraday's law.

**Keywords**: aluminosilicate electrolyte, kinetics, steam splitting, thermodynamics

## Introduction

In recent years, much interest has been shown in hydrogen as a potential source of clean energy. Decomposition of water utilizing thermal energy such as that derived from solar heat, nuclear heat or industrial waste heat is the most effective means for obtaining a large quantity of hydrogen cheaply. However, in order to utilize such thermal energy, a means must be found to decompose water at a mild temperature (<900°C) because the free energy inversion temperature of thermal splitting of water vapor (steam) is as high as 4100°C.

There have been many reports on ways of obtaining hydrogen from water in a mild temperature range by using reductants such as $CH_4$ (natural gas), CO and C (coke), so-called steam-reforming reactions, represented by the redox pairs of Eqs 1–3, respectively:

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[*] This paper was presented at the Second International Symposium on the New Frontiers of Thermal studies of Materials, Yokohama, Japan, November, 2001.

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*1418–2874/2002/ $ 5.00*

*Akadémiai Kiadó, Budapest*
*Kluwer Academic Publishers, Dordrecht*

$$2H_2O+CH_4 \rightarrow 4H_2+CO_2, \quad (1)$$

$$H_2O+CO \rightarrow H_2+CO_2, \quad (2)$$

$$2H_2O+C \rightarrow 2H_2+CO_2 \quad (3)$$

These reactions can be designed on the basis of electrochemical microcell models that have been proposed for Wacker-type oxidation of ethylene and the reverse–Boudard reaction in a $Na_2CO_3$ medium [1]. However, these reforming reactions have a serious disadvantage in terms of emission of $CO_2$.

Attempts at direct decomposition of water (hereafter denoted as splitting reaction), typical examples of which are Mark cycle [2], IS cycle [3] and UT cycle [4], which are constructed by making up a set of redox reactions between a catalyst and substrate and, at the same time, by separating the redox sites in order to prevent the recombination of $H_2$ and $O_2$, have also been reported. Although these are still remained at basic research, the process has a great advantage over the above reforming reactions in no $CO_2$ emission.

We describe here a novel system using a potassium aluminosilicate electrolyte under applied potential that is able to split water (or $OH^-$) into $H_2$ and $O_2$ (or $O_2^{2-}$) with a higher yield than the value deduced from Faraday's law, probably by absorbing thermal energy individually in each of the following endothermic steps: dehydration at a temperature below 100°C (step I), disproportionation of KOH ($2KOH \rightarrow H_2+K_2O_2$) at a temperature around 200°C (step II), and disproportionation of $K_2O$ ($2K_2O \rightarrow 2K+K_2O_2$) (step III) at a temperature above 500°C. So-called Nemca [5] (Non-faradic electro-chemical modification of catalytic activity) might be caused in the course of step III, since the rate of hydrogen was ca $10^2$ times larger than the value deduced from Faraday's law.

## Experimental

### *Apparatus*

Quantities of generated gases and cell current under applied voltage were simultaneously measured at a constant temperature or as a function of temperature using a GC and a potentiostat, respectively. (Typical reaction conditions: flow rate of $H_2O$/Ar, 35 $cm^3\ min^{-1}$ at 25°C; applied potential 2–12 V; cell current, 1 $\mu$A–20 mA). Partial pressure of $H_2O$, 24 Torr deduced from equilibrium pressure of water at 25°C.

### *Physical measurements*

$K_2O$ – doped solid electrolytes before and after the reaction were analyzed and identified by TG, XDR-SEM and EPMA, and the gas phase products were analyzed and identified using GC-MS or UV for the bubbling gas through a solution.

### *Catalytic cell preparation*

A catalytic cell consisting of a solid electrolyte and electrodes was made by filling an equimolar mixture of activated $Al_2O_3$, $SiO_2$ and $K_2CO_3$ with other additives if necessary or by filling commercial ceramic wool with the composition of $Al_2Si_2O_7$ into an alumina mold equipped with the electrodes (Pt mesh) and then heating to 950°C and sintering for 24 or 48 h. The resulting porous products were soaked in aqueous solution of $K_2SiO_3$ (assay as $K_2O$: 8%) to be impregnated with $H_2O$, $K^+$ and $OH^-$. The device of the catalytic cell (Fig. 1) and schematic preparation of the catalysts are represented as follows:

Catalyst I: $K_2CO_3$, $SiO_2$ and $Al_2O_3$→950°C (24 h) → R.T. (in $K_2SiO_3$ *aq*) →dried at 50°C (in air)

Catalyst II: $K_2CO_3$, $SiO_2$ $Al_2O_3$ and MgO→950°C (48 h)→no impregnation

Catalyst III: commercial ceramic wool→950°C (12 h)→R.T. (in $K_2SiO_3$ *aq*)→dried at 50°C (in the air).

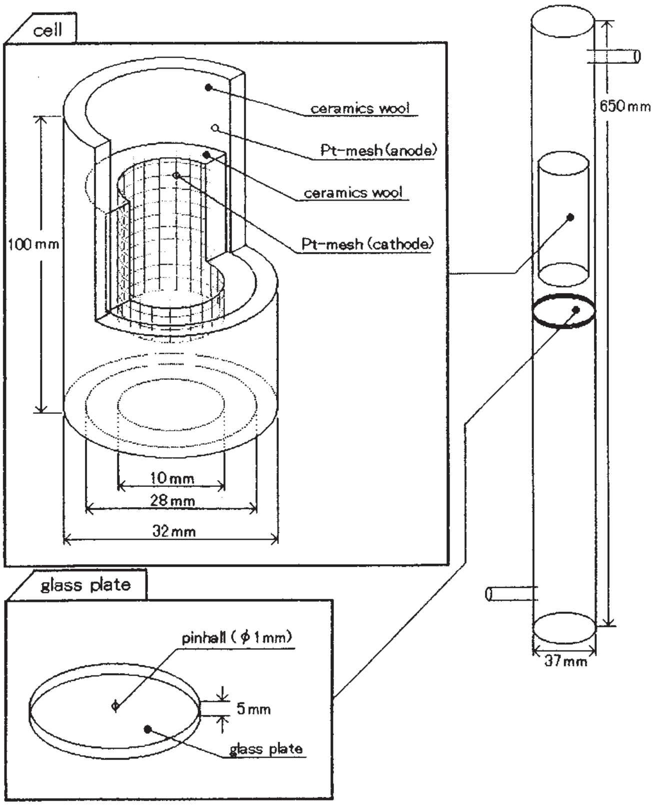

**Fig. 1** The experimental device used for a catalytic cell. Typical reaction conditions: flow rate of $H_2O$/Ar, 35 $cm^3$ $min^{-1}$ at 25°C; applied potential, 2–12 V; cell current, 1 μA–20 mA

## Results and discussion

### *Hydrogen generation in step I*

The rate of generation of hydrogen ($R_{H_2}$) and cell current ($I$) were measured as a function of temperature over a catalyst as a function of temperature with a heating rate of 1°C min$^{-1}$ (Fig. 2) and the kinetic run over Catalyst II at 25°C (Fig. 3). Figure 2 shows that both and $I$ increased with an increase in temperature and reached maximum values at a temperature around 90°C, although these profiles were dependent on $P_{H_2O}$.

Kinetic run in Fig. 3 over Catalyst II indicates that $R_{H_2}$ was maintained constant with the reaction time differently from that the other catalysts, in general, decreased in both $R_{H_2}$ and $I$ with the lapse of time. The observed steady rate in Catalyst II may indicate that MgO in Catalyst II can make the cell porous and consequently the cell can uptake steam even under such low pressure of $H_2O$ as 24 Torr.

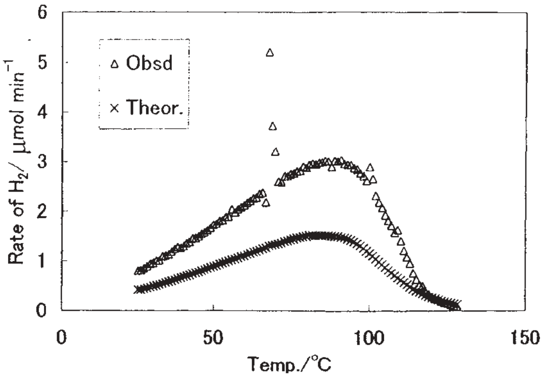

**Fig. 2** Temperature-programmed profile of over Catalyst I under constant applied potential (5 V). θ=1°C min$^{-1}$. Flow rate of $H_2O$/Ar= 40 cm$^3$ min$^{-1}$ at 25°C

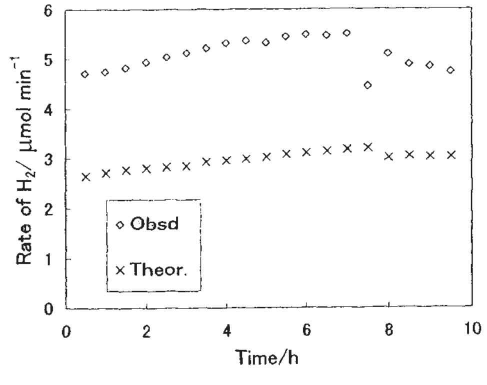

**Fig. 3** Kinetic runs over Catalyst II at constant temperature (25°C) and voltage (2 V). Flow rate=45 cm$^3$ min$^{-1}$

The theoretical curve in the figures denotes the value of $R_{H_2}$ deduced from the cell current using Faraday's law. The decreasing tendency of $R_{H_2}$ at temperatures above 90°C was due to the progress of dehydration of the cell. (The anhydrous cell was an insulator). The differences between the observed and theoretical values of $R_{H_2}$ suggest that the energy ($\Delta H$) needed for steam splitting can be derived from both electrical energy and thermal energy, the latter of which may originate in the endothermic process of the dehydration.

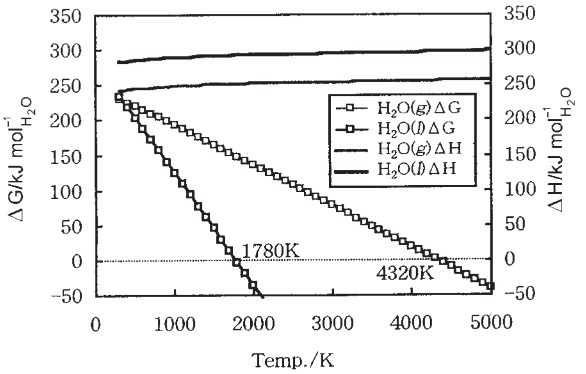

**Fig. 4** Thermodynamical relationships of $\Delta G = \Delta H - T\Delta S$ for steam and water system, assuming the stoichiometry of $H_2O(g \text{ or } l) \rightarrow H_2(g) + 1/2O_2(g)$

Figure 4 shows the thermodynamical relationships of $\Delta G = \Delta H - T\Delta S$ for steam and water, respectively, where $\Delta G$ and $T\Delta S$ mean electrical energy and thermal energy, respectively. It should be noted that the observed contribution of thermal energy was much greater than the estimated value from the thermodynamical requirement, suggesting that the reaction can be governed kinetically when recombination of $H_2$ and $O_2$ is prevented.

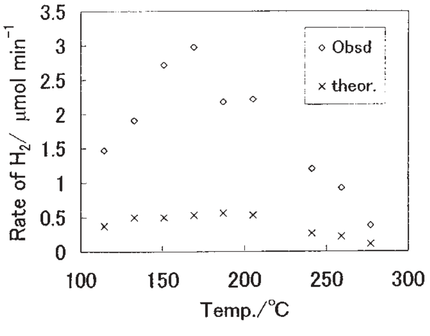

**Fig. 5** Temperature-programmed profile over Catalyst III under a constant voltage (5 V). $\theta = 0.5$°C min$^{-1}$

### *Hydrogen generation in step II*

Upon further heating, the rate of $H_2$ generation increased again and became maximum at a temperature around 170°C. Figure 5 shows the temperature-programmed profile over Catalyst III, and the TG-DTA curves of Catalyst III are shown in Fig. 6. It should be noted that the observed maximum value of was ca six-times greater than the theoretical value from Faraday's law and that a very strong endotherm appeared near the maximum temperature on the DTA curve.

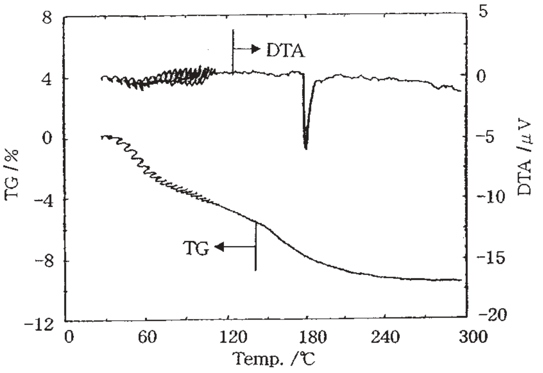

**Fig. 6** TG and DTA curves of Catalyst III in an Ar atmosphere $\phi=1°C\ min^{-1}$

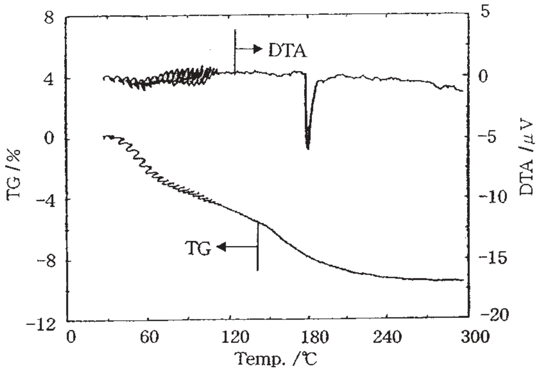

**Fig. 7** Kinetics of $H_2$ at 200°C and 3.2 V over Catalyst III

Interestingly it was found that KOH and also other hydroxides of the first- and second-group metals began to generate $H_2$ upon heating at a temperature around 200°C in an inert atmosphere, and the quantities of $H_2$ tended to increase with an increase in the difference between the enthalpy of formation of normal oxide and that of peroxide $\Delta(\Delta H_f)$ (Table 1), suggesting a novel reaction represented by Eq. (4).

$$2KOH \rightarrow K_2O_2 + H_2 \qquad (4)$$

**Table 1** Standard heat of formation ($\Delta H_f$) of abnormal oxides and the differences in $\Delta H_f$ between the normal and abnormal oxides ($\Delta(\Delta H_f)$ of first- and second-group metals

| Metals | Total $H_2$ generation per 1 mol of hydroxide/mmol | $\Delta H_f$/kJ mol$^{-1}$ | $\Delta(\Delta H_f)$/kJ mol$^{-1}$ |
|---|---|---|---|
| Li | 2 | –632.6[a] | –33.9[d] |
| Na | 5 | –513.2[a] | –95.2[d] |
| K | 15 | –495.4[b] | –133.4[d] |
| Rb | 15 | –278.7[a] | 60.3[e] |
| Cs | 26 | –520.1[c] | –174.1[f] |
| Mg | 1.4 | – | – |
| Ca | 3 | –652.7[a] | –17.6[d] |
| Sr | 2.4 | –633.5[a] | –41.4[d] |
| Ba | 23 | –634.3[a] | –80.8[d] |

[a]Peroxide; [b]$RbO_2$; [c]$Cs_2O_3$; [d]$\Delta H_f$ (peroxide) – $\Delta H_f$ (oxide); [e]$\Delta H_f$ ($RbO_2$) – $\Delta H_f$ ($Rb_2O$); [f]$\Delta H_f(Cs_2O_3)$ – $\Delta H_f(Cs_2O)$

The formation of peroxide ion was confirmed on the basis of specific IR peak of $O_2^{2-}$ at around 890 cm$^{-1}$ and the formation of $H_2O_2$, on the basis of specific coloration by trapping the evolved gas in 15% $TiCl_4$ –4N $H_2SO_4$, and the formation of $K_2$, on the basis of MS peak at 78. Therefore reaction (4) can be followed by the decomposition of $H_2O_2$ into $H_2O$ and $O_2$, and at high $P_{H_2O}$, $K_2O$ can possibly change into KOH. The experimental results (Fig. 7) may support the above catalytic scheme.

*Hydrogen generation in step III*

When steam passed through the systems shown in Fig. 7, $R_{H_2}$ significantly increased at a temperature around 500°C for metals such as Na, K and Cs, whose oxides are known to undergo a disproportionation into their peroxides, and for metals at a temperature around 400°C [6]. Thus, we assumed the catalytic reaction, comprised of the following three reactions:

$$M_2O \rightarrow M_2(g)+M_2O_2, \tag{5}$$

$$M+H_2O \rightarrow H_2+M_2O, \tag{6}$$

$$M_2O_2+H_2O \rightarrow M_2O+H_2O_2 \text{ (or } H_2O+1/2O_2), \tag{7}$$

Since reaction (5) is a strong endothermic process ($\Delta H$=354 kJ mol$^{-1}$, for K) with a high entropy change, it seems likely that a thermal process is greatly superior to an electrical process in providing $\Delta H$ (342 kJ mol$^{-1}$) of steam splitting. The experimental results show that was ca $10^2$ times larger than the value estimated from Faraday's law, although the absolute value of $R_{H_2}$ was strongly dependent on $P_{H_2O}$. This may be due to the fact that the quantity of adsorbed $H_2O$ is very low at such high temperature (above 500°C). Thus, the reaction should be performed at high $P_{H_2O}$.

The present work was supported by the Jaeri's Nuclear Research Promotion Program. We thank Prof. K. Asami (Laboratory for Developmental Research of Advanced Materials, Institute for Material Research, Tohoku University) for the EPMA and GC-MS measurements and Prof. N. Morita (Graduate School of Science, Tohoku University) for helpful discussion.

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