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Thermochemical two-step water splitting cycle using Ni-ferrite and CeO$_2$ coated ceramic foam devices by concentrated Xe-light radiation

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Abstract

Nickel ferrite (NiFe$_2$O$_4$) and pure cerium oxide (CeO$_2$) supported on monoclinic zirconia (NiFe$_2$O$_4$/m-ZrO$_2$) are proposed as promising redox materials for the production of hydrogen from water via a thermochemical two-step water splitting cycle. Ceramic foam devices coated with NiFe$_2$O$_4$/m-ZrO$_2$ or pure CeO$_2$ particles are prepared as a receiver/reactor operating a thermochemical water splitting cycle to produce hydrogen. The foam devices are examined in a directly irradiated receiver/reactor by a sun simulator on a laboratory scale. The purpose of this study is to examine the evolution of oxygen and hydrogen during the cyclization reaction different thermal-reduction (T-R) temperatures of 1450 and 1550 °C, and to compare the reproducible and stoichiometric oxygen/hydrogen production for both foam devices through a repeatable two-step reaction. In this study, a zirconia ceramic foam was used as a matrix for the reacting materials of NiFe$_2$O$_4$/m-ZrO$_2$ or CeO$_2$ particles. The zirconia ceramic foam has a diameter of 60 mm, a thickness of 15 mm, and a porosity of 10 cpi (cell number per linear inch). The loading amounts of reacting materials are 5 wt% for NiFe$_2$O$_4$/m-ZrO$_2$ and 40 wt% for CeO$_2$ particles. A concentrated Xe-beam is radiated to the foam device in a N$_2$ stream for the T-R step and in a N$_2$/steam gas mixture for the subsequent water-decomposition (W-D) step.

Keywords: Hydrogen production; Water splitting cycle; Solar concentrating heat; Ceramic foam; Ferrite
1. Introduction

Various processes by a multi-step thermochemical water splitting cycle have been proposed and demonstrated for the purpose of converting concentrated high-temperature solar heat into clean hydrogen in sunbelt or solar-belt regions [1]. The simplest process is a thermochemical two-step water splitting cycle by a metal-oxide redox pair. Thermochemical two-step water splitting cycle by an iron oxide redox pair was first proposed by Nakamura [2].

\[
\begin{align*}
\text{Fe}_3\text{O}_4 & \rightarrow 3\text{FeO} + 1/2\text{O}_2 & \text{thermal reduction, or T-R step} \\
\text{H}_2\text{O} + 3\text{FeO} & \rightarrow \text{Fe}_2\text{O}_4 + \text{H}_2 & \text{water decomposition, or W-D step}
\end{align*}
\]

One of the major problems for this cycle, however, is the rapid deactivation of iron oxide particles in the cyclization reaction. This is due to the high-temperature melting and sintering of the iron oxide particles. There were no reports that demonstrated high activity and good repeatability of the cyclization two-step water splitting using iron-based oxide (ferrite) particles before the present authors first demonstrated a repeatable two-step water splitting cycle by highly active zirconia-supported ferrites in 2003 [3]. In that study, the T-R and W-D steps could be performed at 1400 and 1000 °C, respectively. Niigata University has been developing the ferrites supported on monoclinic zirconia–m-ZrO$_2$ and on yttrium-stabilized cubic zirconia–c-YSZ as the working redox materials for the thermochemical cycle [1]. However, cerium oxide has recently emerged as a promising reactive redox material for a thermochemical two-step water splitting cycle [4]. The redox cycle using cerium oxide allows higher melting points for the oxides, leading to good sintering resistance and superior cyclization reactivity by itself with no support materials at high temperature. However, it has been reported that cerium oxide can form a compound at a thermal reduction (T-R) temperature that is less than 2000 °C. This compound represents a non-stoichiometric state in oxide between CeO$_2$ and Ce$_2$O$_3$. Because the compound requires a relatively lower reduction temperature, the volatility is decreased [4-6]. A repeatable two-step water splitting cycle using CeO$_2$/CeO$_{2.5}$ is represented by

\[
\begin{align*}
\text{CeO}_2 & \rightarrow \text{CeO}_{2.5} + \delta/2\text{O}_2 & \text{T-R step} \\
\text{CeO}_{2.5} + \delta\text{H}_2\text{O} & \rightarrow \text{CeO}_2 + \delta\text{H}_2 & \text{W-D step}
\end{align*}
\]

CeO$_{2.5}$ represents a non-stoichiometric state of cerium oxide that is formed during the T-R step and oxygen is released from the CeO$_2$. The CeO$_{2.5}$ is sufficiently reactive as the redox material for water decomposition step. In the W-D step, the CeO$_{2.5}$ can react with water vapor at temperatures less than 1000 °C to produce hydrogen.

Solar chemical receivers/absorbers or reactors with ferrite and cerium oxide particles have been developed and tested worldwide for hydrogen production from water using concentrated solar radiation as an energy source [1]. The solar chemical reactors are equipped with a transparent quartz window that passes concentrated solar radiation to directly heat the redox materials. Zirconia-supported ferrites were used as a redox material for a solar water splitting cycle reactor, CR5, by Sandia National Laboratories [7]. Also, a volumetric solar reactor, wherein the solar receiver/absorber has a multichannel ceramic honeycomb coated with ferrite particles as the redox material, has been demonstrated in the EU HYDROSOL project [8].

Niigata University has developed ceramic foam devices whose foam matrix is made of MgO-partially stabilized zirconia (MPSZ). The MPSZ foam matrix has superior characteristics as compared with SiSiC and SiC[9], including high heat resistance and chemical inertness with iron oxide at high temperature. Also, the foam structure can effectively absorb light irradiation owing to its large specific surface area. These foam devices were possible for multicycling the two-step water splitting process [10-13]. Niigata University started an international project for solar two-step water splitting cycle using foam device reactor: a joint research project between Niigata University (Japan) and Inha University (Korea), started in autumn 2008. The reactive water splitting foam device was developed and prepared by Niigata University, and involves coating a zirconia foam with reactive, zirconia-supported ferrite particles [14]. The objectives of the project are to develop reactive foam devices with ferrite as the working material, to design and fabricate a windowed solar reactor with the reactive foam device, and finally, to demonstrate its performance in sunlight with a 5 kWth dish-type solar concentrator [15]. Recently, a new joint project on the solar demonstration of water splitting reactor using foam device of NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ and CeO$_2$/MPSZ was started between Niigata University (Japan) and– Korean Institute of Energy Research, KIER (Korea). The project aims to
develop a novel-type of solar water splitting reactor with reactive cerium- or iron oxides-coated foam devices to produce solar hydrogen from water, and to demonstrate its performances sunlight with a 45-kWth solar furnace.

In this study, CeO$_2$/MPSZ foam devices were prepared by the spin-coating method. A thermochemical two-step water splitting cycle using the CeO$_2$/MPSZ foam devices were tested and the results are reported here for the first time. Further, the reproducible and stoichiometric oxygen/hydrogen production for CeO$_2$/MPSZ foam device was compared with activity of the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ foam device through a repeatable two-step reaction. The present authors examine the evolution of oxygen and hydrogen the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ and CeO$_2$/MPSZ foam devices during the cyclization reaction with thermal-reduction (T-R) temperatures of 1450 and 1550 ºC in a windowed single reactor by Xe-beam irradiation to simulate solar radiation. A comparison of the reproducible and stoichiometric oxygen/hydrogen production for both foam devices through a repeatable two-step reaction is also made.

2. Preparation of NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ and CeO$_2$/MPSZ foam devices

Zirconia-supported nickel ferrite was prepared as follows. Monoclinic zirconia (m-ZrO$_2$) was used to support NiFe$_2$O$_4$. The monoclinic zirconia had a purity of 98 %, a particle size smaller than 1 μm, and a Brunauer-Emmett-Teller (BET) relative surface area of 13 m$^2$/g, whereas the c-YSZ (provided by Tosoh corporation) support had a purity of 99%, a particle size smaller than 1 μm and the BET relative surface area of 7 ± 2 m$^2$/g. The m-ZrO$_2$-supported NiFe$_2$O$_4$ was prepared by coating the m-ZrO$_2$ particles with NiFe$_2$O$_4$ using aerial oxidation of aqueous suspensions of Fe(II) hydroxide with Ni(II) hydroxide [16]. The loading of NiFe$_2$O$_4$ in the m-ZrO$_2$-supported NiFe$_2$O$_4$ was approximately 15 wt%.

Figures 1(a) and (b) show representative photographs of the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ foam devices irradiated for the T-R step at 1450 and 1550 ºC respectively. The devices were prepared by using the spin-coating method [14, 17]. The matrix of the ceramic foam devices was made of MPSZ (provided by Foseco Japan Ltd). The foam matrix had a diameter of 60 mm, a thickness of 15 mm, and a cell size of 10 cpi (cell number per linear inch). The disk-shaped foam matrix was impregnated with a ferrite-containing slurry consisting of 10 g of NiFe$_2$O$_4$/m-ZrO$_2$ powder, 33 mL of distilled water, 0.1 g of dispersant (sodium polyacrylate), and 0.1 g of binder (acrylic resin). The impregnation process was performed under reduced pressure in order to remove bubbles of air contained inside the foam and to coat the MPSZ foam homogeneously. The impregnated MPSZ foam was set in a spin coater and rotated at rates of 600 -1000 rpm (10-17 s$^{-1}$) in order to remove excess slurry on the foam. After rotation, the foam was heated to 1100 ºC and the foam device was calcined for 1 h in an air stream. This process of spin coating was repeated approximately 15 times. Subsequently, the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ foam device was calcined at 1100 ºC for 1 h in an air stream. The loading amount of the NiFe$_2$O$_4$/m-ZrO$_2$ powder was estimated from the weight difference before and after loading. The NiFe$_2$O$_4$/m-ZrO$_2$ loading and weight of the two samples prepared are listed in Table 1.

Representative photographs of the CeO$_2$/MPSZ foam devices are shown in Figures 1(c) and (d). The ceria powder (99.9% purity) was purchased from Kojundo Chemical Laboratory Co., Ltd. The ceria-containing slurry consisted of 10 g of CeO$_2$ powder, 33 mL of the distilled water, 0.1 g of dispersant (sodium polyacrylate), and 0.1 g of binder (acrylic resin). The CeO$_2$/MPSZ foam devices were prepared by the same method as the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ foam devices. After fabrication, the CeO$_2$/MPSZ foam devices were calcined at 1350 ºC for 1 h in an air stream. The CeO$_2$ loading and weight of the foam devices prepared are listed in Table 2.

<table>
<thead>
<tr>
<th>Table 1. NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ foam device information</th>
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<tr>
<td>Sample</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>No.A1</td>
</tr>
<tr>
<td>No.A2</td>
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Table. 2. CeO$_2$/MPSZ foam device information

<table>
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<tr>
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<th>Sample No.B1</th>
<th>Sample No.B2</th>
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<tbody>
<tr>
<td>Weight of foam device /g</td>
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<td>47.6</td>
</tr>
<tr>
<td>CeO$_2$ loading on foam device /wt%</td>
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<tr>
<td>CeO$_2$ loading amount /g</td>
<td>19.9</td>
<td>18.9</td>
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Fig. 1. Representative photographs of the prepared foam devices directly irradiated: NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ at (a) 1450 ºC and (b) 1550 ºC and CeO$_2$/MPSZ at (c) 1450 ºC and (d) 1550 ºC.

3. Cyclization tests of NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ and CeO$_2$/MPSZ foam devices by sun-simulator

Figure 2 (a) shows the experimental set-up of the reactor used to carry out two-step water splitting cycle using the NiFe$_2$O$_4$/m-ZrO$_2$/MPSZ and CeO$_2$/MPSZ foam devices. The reactor was composed of SUS310S metallic tubes, which served as the reactor body and as support for the foam devices, and the foam devices. The foam devices placed on the SUS310S bars fixed inside the reactor were alternately subjected to the T-R and W-D steps. In this series of experiments, two-step water splitting cycle using the foam devices was performed by direct irradiation without preheating of the foam device. The temperature of the foam device was measured by using a B-type thermocouple at the center position of the light-irradiated surface ($T_{center}$). In figure 2 (b), this reactor was placed below three 6 -kW Xe -arc lamps acting as a sun -simulator (SFS-6003A, Nihon Koki) with the central axis of the reactor aligned with the axis of the oval concentrator of the sun -simulator. The concentrator of the sun -simulator reflected the Xe -lamp beam downwards to the focal spot. The surface of the foam device was set on the focal spot of the concentrated light irradiation. The diameter of the focal spot was fixed at 6 cm. The flux intensity of the Xe -lamp beam spot was previously measured using a heat flux transducer with a sapphire window attachment (64-1000-20/SW-1C-150, Medtherm).

The concentrated Xe -light was irradiated in a N$_2$ (purity: 99.999 %) gas stream injected from beside the foam device at 2 dm$^3$/min in order to perform the T-R step. The temperature of the foam device ($T_{center}$) was controlled to 1450 and 1550 ºC during the T-R step by using a B-type thermocouple. This step was continued until oxygen production was finished. After the T-R step, the input energy of the Xe-lamp beam was decreased and the gas
stream introduced into the reactor was changed from N\textsubscript{2} gas to a H\textsubscript{2}O/N\textsubscript{2} gas mixture for the W-D step. The H\textsubscript{2}O/N\textsubscript{2} gas mixture was prepared as follows: liquid water was supplied to spiral steam generator by peristaltic pump with a constant rate of 4 mL/min to generate steam. The generated steam was injected to the reactor together with carrier N\textsubscript{2} gas of 0.5 dm\textsuperscript{3}/min. The thermally reduced foam device was subjected to steam until hydrogen production was finished. The temperature of the foam device for the W-D step was controlled to 1100 °C. The T-R and W-D steps were alternately repeated seven times. After the W-D step in each cycle, the hydrogen and steam remaining in the reactor was exhausted by passing N\textsubscript{2} gas through the reactor for 10 min.

An aliquot of the effluent gas from the reactor was passed through a capillary tube and introduced into a residual gas analyzer mass spectrometer (RG–102P, Ulvac) in order to evaluate the oxygen composition of the product gases and the production rates of oxygen. During the T-R step, variations in oxygen partial pressure in the product gases were measured with respect to reaction time, and the amounts of oxygen evolved were determined from the profile of oxygen partial pressures. The mass spectrometer used was equipped with a standard oxygen gas tank that can supply oxygen gas at a constant flow rate. The oxygen releasing equipment was used to calibrate the relationship between partial pressure and the amount of oxygen evolved.

A part of the effluent gas was divided and the hydrogen concentration in the effluent gas was determined by gas chromatography (GC; GC-8A, Shimadzu) using a thermal conductivity detector (TCD) and residual gas analyzer mass spectrometer (RG–102P, Ulvac). In addition to supplying, the mass spectrometer used was equipped with a standard hydrogen gas tank that can supply hydrogen gas at a constant flow rate. The amount of hydrogen evolved during the W-D step was determined from the profile of hydrogen production.

Fig. 2. (a) Experimental setup of two-step water splitting cycle using quartz window reactor, (b) photograph of quartz windowed solar reactor irradiated using the sun-simulator.

4. Results and discussion

4.1 Cyclization two-step water splitting using thermal-reduction (T-R) temperature of 1450 °C

Samples No. A1 (NiFe\textsubscript{2}O\textsubscript{4}/m-ZrO\textsubscript{2}/MPSZ) and No. B1 (CeO\textsubscript{2}/MPSZ) were directly irradiated for the T-R step at 1450 °C and then heated for the subsequent W-D step at 1100 °C. Figures 3 (a) and (b) shows the oxygen and hydrogen profiles in the first cycle for sample No. A1 and No. B1. The production rates of oxygen and hydrogen per gram of devices (including NiFe\textsubscript{2}O\textsubscript{4}, m-ZrO\textsubscript{2}, CeO\textsubscript{2} and MPSZ matrix) in the first cycle are plotted against the
reaction time. The oxygen release rate from the T-R step of the first cycle rapidly increased at 1200 °C, and attained a maximum rate of approximately 0.025 mL/min·g-NiFe₂O₄/m-ZrO₂/MPSZ device and 0.015 mL/min·g-CeO₂/MPSZ device for samples No. A1 and No. B1 respectively. After reaching the maximum rate, the oxygen release during the T-R step quickly decreased to approximately zero at reaction times of 15-20 min. The oxygen release rate was higher for the NiFe₂O₄/m-ZrO₂/MPSZ foam device than that for the CeO₂/MPSZ foam device. In addition, the oxygen release for the NiFe₂O₄/m-ZrO₂/MPSZ foam device was finished in a short period of time as compared to the CeO₂/MPSZ foam device. Figure 3 also exhibits the hydrogen production rate per gram of devices over time during the W-D step in the first cycle of the repetition test. The maximum rates of hydrogen production during the W-D step of the first cycle were 0.025 mL/min·g-NiFe₂O₄/m-ZrO₂/MPSZ device and 0.04 mL/min·g-CeO₂/MPSZ device at 1100 °C. After reaching the maximum rate, the hydrogen production during the W-D step gradually decreased to approximately zero at reaction times of 20-40 min. The hydrogen production rate was higher for the CeO₂/MPSZ foam device than for the NiFe₂O₄/m-ZrO₂/MPSZ foam device. The amount of oxygen release at the first cycle was 4.9 and 4.7 mL for the NiFe₂O₄/m-ZrO₂/MPSZ foam device and the CeO₂/MPSZ foam device, respectively. The amount of hydrogen production was 6.7 and 15 mL for the NiFe₂O₄/m-ZrO₂/MPSZ foam device and the CeO₂/MPSZ foam device, respectively.

Figure 4 shows the variations in the amount of oxygen and hydrogen produced per gram of device during the repeated T-R and W-D step for samples No. A1 and No. B1. The oxygen release for sample No. A1 was approximately 3.9 mL/device without significant fluctuation throughout the cyclization reaction. The oxygen release for sample No. B1 was 4.7 -13.2 mL/device over the seven cycles. These results show that sample No. B1 is capable of releasing a greater amount of oxygen than sample No. A1 at the T-R step temperature of 1450 °C. As seen in Figure 4, the hydrogen production for the sample No.A1 was unstable between 2.7 -13 mL/device throughout the cyclization reaction. The behavior initially increased up to the third cycle but decreased after the fourth cycle. The reason for the decrease in hydrogen production is the sintering of the NiFe₂O₄/m-ZrO₂ particles. The hydrogen

![Sample No.A1](image1)

![Sample No.B1](image2)

Fig. 3. Oxygen and hydrogen profiles in the first cycle for samples (a) No. A1 (NiFe₂O₄/m-ZrO₂/MPSZ) and (b) No. B1 (CeO₂/MPSZ).
production for sample No. B1 was 15-23 mL/device over the seven cycles. The fluctuating production of hydrogen means that sample No. B1 exhibited relatively good reproducibility of hydrogen production when the T-R step was performed at a temperature of 1450 °C. Also, the hydrogen production was higher for sample No. B1 than for sample No. A1 throughout the cyclization reaction. In samples No. A1 and No. B1, the H₂/O₂ ratio of each cycle was not exactly 2:1; instead, the H₂/O₂ average ratios over seven cycles were 1.9 and 2.0, respectively. This is because either the heat flux of the simulator changed slightly or because the steam did not come into good with the device surface in each cycle. Because the redox materials of NiFe₂O₄/m-ZrO₂ and CeO₂ were coated on the matrix, it was difficult to examine the reactivity and stoichiometry of the redox materials through the entire cyclic reaction.

Fig.4. Variations in the amount of oxygen and hydrogen produced per gram of device during the repeated (a) T-R and (b) W-D steps for samples No. A1 (NiFe₂O₄/m-ZrO₂/MPSZ) and No. B1 (CeO₂/MPSZ).

4.2 Cyclization two-step water splitting using thermal-reduction (T-R) temperature of 1550 °C

Samples No. A2 and No. B2 were directly irradiated for the T-R step at 1550 °C and then heated for the subsequent W-D step at 1100 °C. Figures 5(a) and (b) shows the oxygen and hydrogen profiles in the first cycle for samples No. A2 and No. B2, respectively. The oxygen release rates during the T-R step of the first cycle were attained to maximum rate of 0.1 mL/min·g-NiFe₂O₄/m-ZrO₂/MPSZ device and 0.07 mL/min·g-CeO₂/MPSZ device for samples No. A2 and No. B2, respectively. The maximum rate for oxygen release increased approximately 4 times in comparison to that at the T-R step temperature of 1450 °C. However, the period of oxygen release was finished at almost the same time as that at 1450 °C. These results show that the release rate of oxygen for both samples increased with increasing T-R step temperature. The maximum rates of hydrogen production during the W-D step of the first cycle were 0.1 mL/min·g-NiFe₂O₄/m-ZrO₂/MPSZ device and 0.13 mL/min·g-CeO₂/MPSZ device for samples No. A2 and No. B2, respectively. The maximum rate for hydrogen production increased approximately 3-4 times in comparison to that at the T-R step temperature of 1450 °C. These results show that the production rate of hydrogen for both samples increased with increasing T-R step temperature. The amount of oxygen release at the first cycle was 28 and 20 mL for samples No. A2 and No. B2, respectively. The amount of hydrogen production was 80 and 88 mL for samples No. A2 and No. B2, respectively.
Figures 6(a) and (b) show the variations in the amount of oxygen and hydrogen produced, respectively, per gram of device during the repeated T-R and W-D steps for samples No. A2 and No. B2. The oxygen released for sample No. A2 was about 29 mL/device through the cyclization reaction. The oxygen release for sample No. B2 was initially 24 mL/device at the first cycle and about 50 mL/device in cycles 2-7. The results for the oxygen production show that sample No. B2 can produce more oxygen in the cyclization reaction than sample No. A2 at the T-R step temperature of 1550 °C. On the other hand, the hydrogen production for sample No. A2 gradually decreased to less than half the original amount. The result for the hydrogen production show that sample No. A2 was deactivated as the cyclization number increased. The reason for this decrease is the sintering of NiFe2O4/m-ZrO2 particles as found at the T-R step temperature of 1450 °C. The T-R temperature of 1550 °C was too high to maintain the activity of sample No. A2. By increasing the T-R temperature from 1450 °C to 1550 °C, the oxygen released for samples No. A1 and No. A2 it was enhanced approximately seven times and for samples No. B1 and No. B2 enhanced about five times. Thus, hydrogen production increased significantly for both samples. In samples No. A2 and No. B2, the H2/O2 ratio of each cycle was not exactly 2:1, as was found samples No. A1 and No. B1. Instead the H2/O2 average ratio seven cycles were 1.7 and 1.9 for samples No. A1 and No. B1, respectively.
CeO₂/MPSZ foam device was successfully prepared by spin coating method. The foam devices were tested in a windowed foam device reactor for a thermochemical two-step water-splitting cycle using a sun-simulator. The oxygen and hydrogen production for the CeO₂/MPSZ foam device was able to continue seven cycles at T-R temperatures of 1450 and 1550 °C. A comparison of the NiFe₂O₄/m-ZrO₂/MPSZ and CeO₂/MPSZ foam devices shows that oxygen and hydrogen production were higher for the CeO₂/MPSZ foam devices than for the NiFe₂O₄/m-ZrO₂/MPSZ form device throughout the cyclic reaction because the NiFe₂O₄/m-ZrO₂/MPSZ form devices were sintered during the T-R step.

References


