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Solar Energy Conversion into $H_2$ Energy Using Ferrites

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Abstract: A cation-excess (Ni,Mn) ferrite $Ni_{0.52}Mn_{0.48}Fe_{2.05}O_{4.0}$ with a single phase was synthesized by heating the mixture of corresponding metal salts and oxide in 5% $O_2$/75% $CO_2$/20% $N_2$ gas mixture for 18h at 1100'C. It could be thermochemically activated to form a cation-excess ferrite $Ni_{0.52(1+8)}Mn_{0.48(1+8)}Fe_{2.05(1+8)}O_{4.0}$ in $N_2$ gas at elevated temperature. The $C_0$ value was 0.031 at 1100'C. The activated (Ni,Mn) ferrite was reacted with water to form $H_2$ gas at 700'C. The process was reversible and could be carried out repeatedly.

1. INTRODUCTION

Solar thermal production of hydrogen by single-step (direct) thermal water dissociation, although conceptually simple, still lacks of an effective technique for separating hydrogen and oxygen at high temperatures. Two-step water-splitting cycle, based upon metal oxides redox system, bypasses the separation obstacle. A novel two-step water-splitting cycle is presented which, in contrast to previously proposed cycles that require upper operating temperatures above 2300K, can be conducted at a much moderate (and workable) temperature. In the first, endothermic step, $Ni_{0.5}Mn_{0.5}Fe_{2}O_{4}$ is thermally activated at above 1073 K to form an oxygen-deficient ferrite. In the second step, activated ferrite is reacted with water at below 1073 K to form hydrogen; the ferrite product is recycled to the first step. $H_2$ and $O_2$ are derived in different steps, eliminating the need for high-temperature gas separation. Both reactions have been experimentally demonstrated using concentrated solar radiation as the energy source for the activation. In a previous paper [1], we described the experimental apparatus and discussed the experimental results. This note summarizes the main findings.

2. EXPERIMENTAL SECTION

(Ni,Mn) ferrite was synthesized by heating $\alpha$-Fe$_2$O$_3$, NiCO$_3$·2Ni(OH)$_2$·4H$_2$O and MnCO$_3$ in requisite quantities in different gas atmospheres at 1273-1373K. The solid phase was identified by X-ray diffraction with CuK$\alpha$ radiation. The Fe$^{2+}$/Fe$^{3+}$ mole ratio of samples was determined by colorimetry using 2,2'-bipyridyl and ICP spectrometry was used to determine the chemical composition. Thermal analyses were conducted using TG-DTA and/or MS. Oxygen releasing and water-splitting reactions were monitored with MS in a low $O_2$-content $N_2$ gas. The oxygen partial pressure was determined to be $1.37 \times 10^{-3}$ Pa using MS intensity ratio of $N_2^{16}$ and $O_2^{18}$ and the NIST data ($N_2^{16}$/N$_2^{18}$=1000/7). The reactions were also demonstrated in experiments conducted at the PSI solar furnace [1]. A charge of 5g of (Ni,Mn) ferrite powder mixed with 7.5g of $Al_2$O$_3$ grains was loaded in the reactor and directly exposed to solar flux intensities over 1000 suns.

3. RESULTS AND DISCUSSION

Synthetic conditions for (Ni,Mn) ferrite were studied in different gas atmospheres. Starting materials were physically mixed using acetone in proportions to give the final composition of $Ni_{0.5}Mn_{0.5}Fe_{2}O_{4}$ and heated at 1273K in $N_2$ (Fig. 1a). The product was admixed with FeO and metallic (Ni,Fe) phases besides the spinel phase. The formed (Ni,Mn) ferrite gave the lattice constant of 0.84284(5) nm. The digit in the parenthesis denotes the standard deviation. The product was then heated at 1373K for 15h in 10% $O_2$/50% $CO_2$/40% $N_2$ gas mixture to oxidize the metallic phase (Fig. 1b). The metallic phase disappeared to form hematite, $NiO$ and the spinel phase. The product was ground thoroughly and heated in 2% $O_2$/8% $CO_2$/8% $N_2$ gas mixture at 1373K. The product was mostly composed of the spinel compound with the lattice constant, 0.84278(5) nm. Finally the product was heated in 5% $O_2$/75% $CO_2$/20% $N_2$ gas mixture at 1373K for 18h to obtain the single phase of NiMnFe$_2$O$_4$ (Fig. 1c). The lattice constant was 0.84175(6) nm. The decrease in the lattice constant indicates...
Figure 1: XRD pattern of the (Ni,Mn) ferrites prepared temperatures of 1273K(Ni3)(a), 1375K(2O2:CO2:N2=0.1:0.5:0.4)(b), and 1375K(2O2:CO2:N2=0.05:0.75:0.2)(c).

Figure 2: Oxygen and hydrogen evolution during activation and water-splitting reactions, using concentrated solar irradiation. O2 evolution (Curve A) and the H2 evolution (B).

Thus, the proposed water-splitting cycle has been demonstrated using solar energy. The above difference in the drawback is the need to provide an oxygen-free atmosphere and the relatively small fraction of oxygen liberated during the activation step (as compared with a reduction step to a lower-valence oxide, e.g., from Fe3O4 to FeO).

The solution of Ni2+ ion. It falls between the lattice constants of Ni(II) ferrite 0.83359(3) nm and Mn(II) ferrite 0.8498 nm, which corroborated the formation of the solid solution. The chemical composition of the (Ni,Mn) ferrite was determined by the thermogravimetry at 873K in H2 stream. The heated sample was identified by XRD to comprise of metallic Ni, Fe and MnO phases. The weight loss and the precise chemical analyses of the (Ni,Mn) ferrite gave a chemical composition, Ni0.52Mn0.51Fe2.05O4.0.

O2 releases from the above-mentioned ferrite samples were studied using the TG-MS measurement in N2 atmosphere. The (Ni,Mn) ferrite showed the maximum release of O2 at 1223K, corresponding to the weight decrease of 0.26%. The weight decrease began at 1073K and was constant at 1373K in N2 atmosphere, and the loss of 0.26% is equal to the cation-excess value (e) of 0.040. On the other hand, Ni(II) ferrite showed a smaller O2 release at 1073K, corresponding to the weight loss of 0.15%. It is smaller than the (Ni,Mn) ferrite. The lattice oxygen release of (Ni,Mn) ferrite was further studied at 1123K-1373K in CO2 atmosphere (PO2 = 8.9 Pa at 1273K). The partial pressure of O2 gas comes from CO2 dissociation and depends on the temperature. Approximately the same O2 release from the (Ni,Mn) ferrite was observed in CO2 and N2 flow. This level of O2 partial pressure did not affect the O2 release from (Ni,Mn) ferrite lattice. The maximum release rate of O2 was found at 1248K and very consistent with the weight loss. The O2 release from (Ni,Mn) ferrite in different atmospheres showed an increased lattice constant depending on the extent of O2 release or value. The crystal structure was retained upon O2 release and the lattice oxygen release could be assumed to be reversible. Then, the (Ni,Mn) ferrite should constitute a redox system and serve as the water splitting. It will be possible by the temperature swing method. At higher temperature than 1173K, the lattice oxygen of (Ni,Mn) ferrite is released to activate for water splitting and the activated (Ni,Mn) ferrite can absorb oxygen of water to split water at lower temperature than 1073K. Thus, the thermochemical cycle produces H2 gas from H2O.

Figure 2 shows the oxygen (curve A) and hydrogen (curve B) signals, monitored by MS. During activation, the reactor was heated to about 1373 K and Ar gas was passed through the sample. Peak I of curve A corresponds to oxygen evolution due to the release of the ferrite lattice oxygen. After the activation was completed, the reactor was cooled to around 773K, and steam/Air mixed gas was passed through the sample for 5 min. Afterwards, the reactor temperature was raised to 773K, 823K, 873K and 973K. A high H2 evolution amount was measured at 973K. The cycling capability of this chemical system was again proved by contiguously repeating both activation and water-splitting steps following the same experimental procedure. Peaks II and III of curve A correspond to the oxygen evolution by re-activating (Ni,Mn) ferrite just after the first cycle. Subsequently, peaks e and f of curve B correspond to the hydrogen evolution from the water-splitting in the second cycle. Thus, the proposed water-splitting cycle has been demonstrated using solar energy. The above difference in the O2 release behavior may be explained based on the crystallographic data of these metal ions. The self-diffusion coefficient of oxide in the Zn ferrite is reported to be 1.6x10-13 cm2 s-1 with the activation energy of 229 kJ mol-1 at 1273K[2]. The self-diffusion coefficient of cation in the ferrite (3.1x10-12 cm2 s-1 for Zn, 1.4x10-11 cm2 s-1 for Fe) is much larger than that of oxide ion in the ferrite. The self-diffusion coefficients for ions in the other ferrites are probably in the same order. Ni2+ ion occupies the B site and its crystal ionic radius is 0.0690 nm. When Mn2+ ions with a larger ionic radius of 0.0830 nm replace Ni2+ ions, the latter cations become more mobile because the void space is available for ions. The enlarged availability may be assured by the expansion of the lattice constant 0.83356(3) nm for NiFe2O4, 0.84175(6) nm for Ni0.52Mn0.51Fe2.05O4.0, 0.8498 nm for MnFe2O4. This chemical system requires a moderate (and more workable) upper operating temperature. However, a drawback is the need to provide an oxygen-free atmosphere and the relatively small fraction of oxygen liberated during the activation step.

References