

Sol-gel Synthesis of Ferrite Foam Materials for H₂ Generation from Water-Splitting Reaction

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ABSTRACT

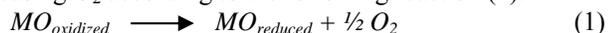
This paper reports the synthesis of Ni-ferrite and Sn-doped Ni-ferrite using sol-gel technique for H₂ generation from water-splitting reaction. In this synthesis, salts of Ni, Sn and Fe were sonicated in ethanol and propylene oxide was added to achieve the gel formation. In the case of Sn-doped Ni-ferrite, polymer microspheres were added prior to the gel formation. As-synthesized gels were aged, dried and then fired rapidly upto 1000°C in a resistive heating furnace or industrial scale microwave furnace and quenched in N₂ environment. The calcined powder was characterized using powder x-ray diffraction, scanning electron microscopy and BET surface area analyzer. Sol-gel derived Ni-ferrite was then used to investigate H₂ from water-splitting reaction at 700°C.

Keywords: Ni-ferrite, Sn-doped Ni-ferrite, sol-gel synthesis, ferrite foam, thermochemical water-splitting.

1 INTRODUCTION

Phase pure ferrites such as NiFe₂O₄ [1], ZnFe₂O₄ [2], MnFe₂O₄ [3] and doped ferrites, for instance, Ni_xMn_yFe₂O₄ [4], Zn_xMn_yFe₂O₄ [5] have application in H₂ generation from thermochemical water-splitting reaction. These ferrites are generally prepared by solid-state mixing, oxidation of aqueous metal hydroxide suspension, self-propagation high temperature synthesis (SHS) and aerosol-spray pyrolysis methods [1,4,6,7]. Although beneficial, there have been reports indicating that these methods sometimes result in chemical heterogeneity, non-stoichiometry, coarser particles and lower specific surface area (SSA). Sol-gel synthesis involving molecular or atomic level mixing and networking of chemical components significantly improves the chemical homogeneity, stoichiometry, phase purity and powder characteristics [8-11]. Because of these advantages, the sol-gel technique is an attractive synthesis approach available for the synthesis of different ferrite materials [12].

A two-step thermochemical water-splitting process seems to be thermodynamically more feasible as it may produce H₂ at significantly lower temperature. In the first step, the metal oxide is reduced at elevated temperatures by releasing O₂ according to the following reaction (1):



In the second step, the reduced metal oxide is oxidized at lower temperature by taking O₂ from water and producing H₂ via water-splitting reaction (2):



Reaction (1) is endothermic (activation/regeneration step) whereas reaction (2) is exothermic (water-splitting step). The combination of one activation/regeneration step and one water-splitting step can be termed as one thermochemical cycle. Typically, the water-splitting reaction requires lower temperatures as compared to that of regeneration step which takes place at relatively higher temperatures, making redox materials to undergo thermal cycling [13]. As a result, potential problems such as grain growth, thermal stress, and eventually spalling of redox material coating may occur in a thermal reactor [14]. This may further clog the reactor and the process lines, which may result in increasing the pressure drop and thereby creating unsafe processing conditions.

The above issues can be addressed if porous or foam ferrite materials are employed for thermochemical water-splitting reaction. These porous materials will have higher SSA which may provide higher number of active sites for water-splitting reactions resulting into higher yields of H₂. Also, the packed-bed reactors loaded with porous ferrites with different morphologies will provide lower pressure drop and minimize resistance for gas transport. Porous ferrite materials can be synthesized using a surfactant templating assisted sol-gel method. In this method the ionic/non-ionic surfactants can be added to the precursor solution prior the gel formation to achieve mesoporous structure with pore size in the range of 2-50 nm. To prepare the ferrite foam material, the precursor solution can be mixed with polymer microspheres (EXPANCEL® from Akzo Nobel) prior the gel formation. Expancel is a free flowing powder of spherical, expanded particles. The interior spherical void contains hydrocarbon gases and the shell is made up of a thermoplastic polymer. When gels containing Expancel microspheres are fired rapidly, foam-like materials with higher SSA can be realized.

Among several ferrites investigated so far, Ni-ferrite was reported to be the most promising material for H₂ production [14]. Fresno et al. [15] reported average H₂ production of 18.02 ml/g/cycle (water-splitting at 1000°C and regeneration at 1500°C) using Ni-ferrite, which was higher than the H₂ produced by other ferrites. Bhosale et al.

[16] reported that the sol-gel derived NiFe_2O_4 (calcined in air) was capable of producing a large volume of H_2 at lower water-splitting and regeneration temperatures of 700°C and 900°C , respectively.

In this paper, Ni-ferrite and Sn-doped Ni-ferrite were synthesized using sol-gel technique. To prepare ferrite foam materials, gels were mixed with Expancel microspheres and heated rapidly upto 1000°C in N_2 environment. The ferrite materials were used to investigate H_2 production from water-splitting reaction at 700°C .

2 EXPERIMENTAL

2.1 Synthesis of Ferrites

In the synthesis, chloride salts of Ni, Sn, and Fe were added in ethanol and sonicated to obtain a clear solution. To this solution, a predetermined amount of propylene oxide (PO) was added and the solution was set aside undisturbed at room temperature until a gel was observed. Gel formation was observed in 5–10 min. To prepare the ferrite foam material, the clear solution was mixed with polymer microspheres (20 wt% of the gel) prior to the gel formation. The gels were aged for 24 h at room temperature, dried at 100°C , heated rapidly upto 1000°C in a resistive heating furnace or industrial scale microwave furnace (VIS 300-01 B, 5kW CPI Company) and finally quenched in N_2 environment.

2.2 Characterization of ferrites

The calcined powders were characterized using X-ray diffraction ($10^\circ \leq 2\theta \leq 80^\circ$ and scanning speed of 2° per minute), scanning electron microscopy (SEM) and BET surface area analyzer.

2.3 Hydrogen generation set-up

The H_2 generation ability of the sol-gel synthesized Ni-ferrite was investigated using the experimental set-up shown in Figure 1. It consists of a tubular packed bed Inconel reactor enclosed in a vertical split furnace (Carbolite Inc., USA). The temperature of the furnace was controlled and regulated precisely with the in-built PID controller. Accurately weighed 5.0 g of Ni-ferrite was packed in the middle section of the tubular reactor with the help of raschig rings and quartz wool. A horizontal tube furnace was provided with a stainless steel tube and it was used as a water vaporizing/preheating set-up. Distilled water from the reservoir was fed to the vaporizing/preheating furnace using a metering pump (Fluid Metering Inc., USA) at the flow rate of 1 ml/min. Water vaporized and the preheated steam obtained was fed to the packed bed reactor with N_2 as a carrier gas. A mass flow meter for N_2 (AALBORG Inc., USA) was mounted on the feed line to control the gas flow rate; a flow rate of about 100 ml/min was randomly selected. The exit gas stream from the packed bed reactor was first cooled down

in a water bath and finally fed to the moisture adsorption column containing anhydrous calcium sulfate purchased from W.A. Hammond Drierite Company Inc., OH, USA. The exit gas stream (mixture of N_2 and H_2) from the adsorption column was continuously monitored using an online H_2 sensor. The sensor provided H_2 concentration in vol% at an interval of 1 sec. The effluent gas stream was burned continuously. The water supply was shut down when the online H_2 sensor indicated a minimum of 0.95 (vol%) concentration level.

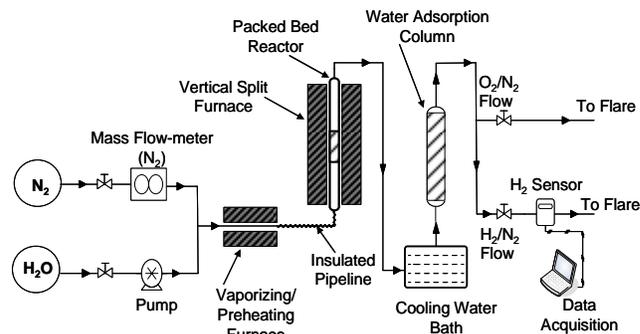


Figure 1: Thermochemical water-splitting reactor set-up for H_2 generation [14].

3 RESULTS AND DISCUSSION

Ni-ferrite gel was synthesized as per the procedure described in Section 2.1. The gels were dried and heated rapidly upto 1000°C in a tube furnace under N_2 environment. The compositional purity of the calcined powder was determined using the powder x-ray diffraction. The XRD pattern presented in Figure 2a indicates a phase composition containing primarily $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ mixed with metallic Ni. The SEM image of the calcined $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ particles is shown in Figure 2b, which indicates faceted grains and broad particle size distribution as both smaller ($<1\mu\text{m}$) and larger ($>2\mu\text{m}$) grains were observed. The SSA of the calcined $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ particles was $0.9\text{ m}^2/\text{g}$.

The H_2 generation ability of $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ was investigated by performing four thermochemical cycles (water-splitting at 700°C and regeneration at 900°C) using the experimental set-up shown in Figure 1. The integrated H_2 volume profile presented in Figure 3 indicates that the amount of H_2 generated by $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ in the 1st water-splitting step at 700°C was 18.84 ml/g. The 2nd, 3rd and 4th water-splitting steps produced 6, 4.5 and 3.7 ml/g of H_2 . It is believed that a major portion of H_2 was routed from water-splitting reaction by the $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$; however, it is also possible that Ni might have undergone redox transition as $\text{Ni}^0 \rightarrow \text{Ni}^{2+}$ and contributed for additional H_2 . A reverse transition of $\text{Ni}^{2+} \rightarrow \text{Ni}^0$, however, may not be possible under the experimental condition employed here as higher water-splitting temperatures have been reported by other investigators for Ni/NiO [17] redox pair in solar thermal reactor for H_2 generation. Overall, an average of 8.37 ml of $\text{H}_2/\text{g}/\text{cycle}$ was observed at the water-splitting temperature

of 700°C. After performing four thermochemical cycles, the ferrite material was analyzed using the BET surface area analyzer. The SSA for the reacted material was 0.39 m²/g. Also, the reacted ferrite was analyzed using powdered X-ray diffraction. We observed a change in phase composition as well as reduction in metallic Ni content.

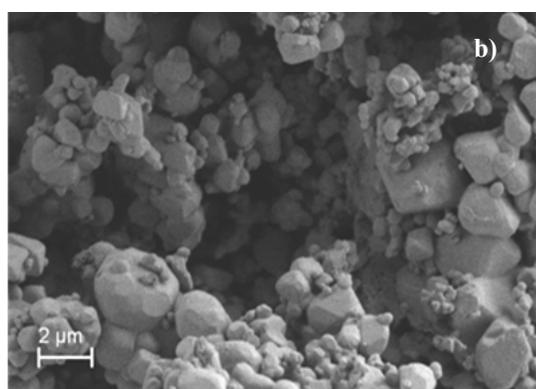
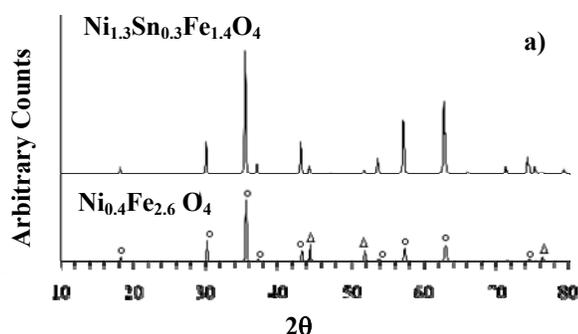


Figure 2: a) XRD patterns of $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ and $\text{Ni}_{1.3}\text{Sn}_{0.3}\text{Fe}_{1.4}\text{O}_4$ calcined at 1000°C in N_2 environment and b) SEM image of calcined $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ (SSA= 0.9 m²/g).

Doping of the ferrites with several metals should increase the O₂ vacancies as compared with the one without any dopant [12]. Using Ni and Mn doped-ferrites, the temperature needed for water-splitting was decreased to 627°C [18]. Thus, it appears that doping is effective in reducing the water-splitting temperature.

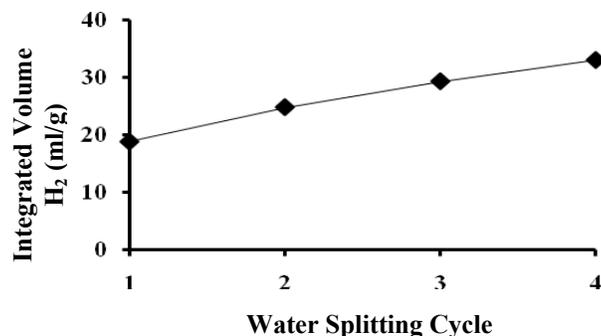


Figure 3: Integrated volume of H₂ generated via water-splitting reaction carried out using $\text{Ni}_{0.4}\text{Fe}_{2.6}\text{O}_4$ at 700°C, in four thermochemical cycles.

Abanades et. al. [19] reported that the complete hydrolysis of Sn is possible at < 550°C. It reflects that Sn could be used as a doping agent in Ni-ferrite, which may lower down the water-splitting temperature. Therefore, Sn-doped Ni-ferrite gel was synthesized using the synthesis method outlined in Section 2.1. The gel was dried at 100°C and rapidly fired upto 1000°C in N_2 environment. The powder x-ray diffraction pattern of the calcined powder as presented in Figure 2a, which represents a phase pure $\text{Ni}_{1.3}\text{Sn}_{0.3}\text{Fe}_{1.4}\text{O}_4$. The SEM image as shown in Figure 4 indicates faceted grains and broad particle size distribution. The BET surface area of calcined $\text{Ni}_{1.3}\text{Sn}_{0.3}\text{Fe}_{1.4}\text{O}_4$ was about 1 m²/g.

The calcined $\text{Ni}_{1.3}\text{Sn}_{0.3}\text{Fe}_{1.4}\text{O}_4$ was used to investigate the H₂ production from water-splitting reaction at 700°C. The preliminary results indicate that this doped ferrite has a great potential to produce H₂ from water-splitting reaction. The experiments are in progress to quantify H₂ production.

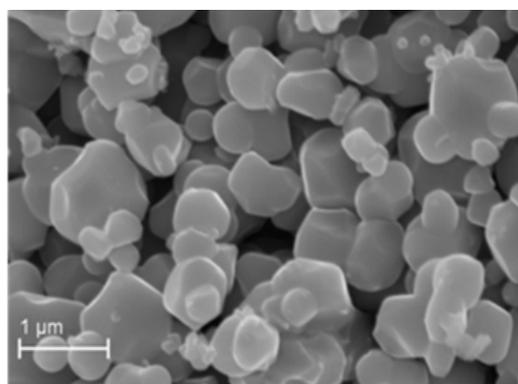


Figure 4: SEM image of $\text{Ni}_{1.3}\text{Sn}_{0.3}\text{Fe}_{1.4}\text{O}_4$ calcined at 1000°C in N_2 environment (SSA=1 m²/g).

It was observed that the calcination of ferrites in N_2 environment results in lower SSA. As mentioned earlier, higher SSA may be advantageous in water-splitting applications because it will provide more number of active sites for water-splitting reactions. If the ferrite is synthesized as a porous material, higher SSA can be achieved. Therefore, during synthesis of Sn-doped Ni-ferrite, about 20 wt% polymer microspheres were added in the precursor solution prior to the gel formation. A well mixed, aged and dried Sn-doped Ni-ferrite gel containing these microspheres was fired rapidly upto 1000°C in N_2 environment in a resistive heating furnace and industrial scale microwave furnace. The SEM images of the two calcined powders are presented in Figure 5a and 5b.

Figure 5a clearly indicates a foam-like morphology with pore size ranging from 50-500 nm. Critical evaluation of few samples under higher resolution showed the presence of the mesopores (2-50 nm) as well. Figure 5b shows fibrous foam-like morphology. After rigorous analysis, we observed that the few fibers in the foam have nano-tubular structure. The BET SSA of these ferrite foams was 156 m²/g, which is significantly higher than that of previously reported ferrites.

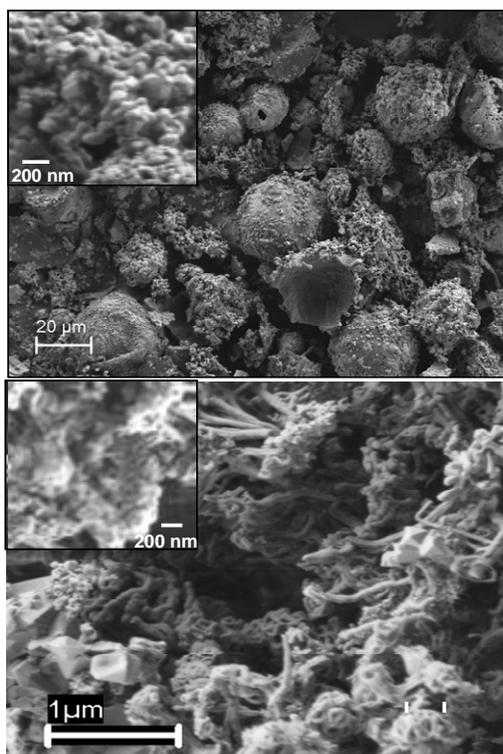


Figure 5: SEM images of Sn-doped Ni-ferrite calcined rapidly at 1000°C in N₂ in a) resistive heating furnace and b) industrial scale microwave furnace.

The investigations are in progress to examine the effectiveness of sol-gel synthesized doped ferrites and ferrite foam materials for H₂ generation using thermochemical water-splitting reactions.

4 CONCLUSIONS

Ni-ferrite and Sn-doped Ni-ferrite were successfully synthesized using sol-gel method involving preparation of a solution containing Ni, Sn and Fe precursors followed by gel formation using propylene oxide and subsequent calcination in N₂ environment. Sol-gel synthesized Ni_{0.4}Fe_{2.6}O₄ was used for H₂ production in four consecutive thermochemical cycles where water-splitting was performed at 700°C and the regeneration was carried at 900°C. In four consecutive thermochemical cycles, Ni_{0.4}Fe_{2.6}O₄ generated about 8.37 ml H₂/g per cycle. Sol-gel technique involving the addition of polymer microspheres in the Sn-doped Ni-ferrite gel produced foam-like or fibrous foam-like morphology. The SSA of this foam-like material was greater than 150 m²/g, which is higher than that of the ferrite materials conventionally used for thermochemical water-splitting reaction. Due to such a higher SSA it is believed that the foam-like material will have tremendous potential for generating H₂ from thermochemical water-splitting reaction.

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