REACTION CHARACTERISTICS OF IRON-DOPED MANGANESE OXIDES FOR SOLAR THERMOCHEMICAL ENERGY STORAGE

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ABSTRACT

High-temperature energy storage is very important for solar power systems with advanced thermal cycles. Manganese oxides are considerable materials for high temperature thermochemical energy storage (800-1000 ℃) due to the merits of low-cost and non-toxic. However, pure Mn_2O_3/Mn_3O_4 redox couple suffers low re-oxidation rate and poor cycling stability. Fe-doped Mn_2O_3 is expected to improve the reaction characteristics, by using a sol-gel synthesis method. The reversibility and cyclic stability are significantly enhanced by the adoption of Fe, verified by over 10 TGA experimental cycles. As to crystallographic analysis, tetragonal spinel and phases cubic spinel were detected in the reduced materials. Jacobsite ($MnFe_2O_4$) is regarded as the vital for the promotion, while $(Mn_{0.8}Fe_{0.2})_2O_3$ exhibits good adaptability under different oxygen partial pressure. Lab-scaled honeycomb materials were investigated for over 100 reduction-oxidation cycles, with an average reaction ratio of 87.9%, which indicates an excellent cyclic stability of iron doped manganese oxides for solar thermochemical energy storage.

Keywords: thermochemical energy storage, metal oxides, reversible reaction

NONMENCLATURE

Abbreviations

CSP	Concentrated Solar Power
XRD	X-Ray Diffusion
TGA	Thermogravimetry Analysis
DSC	Differential Scanning Calorimetry

1.   INTRODUCTION

The growing demand for energy utilization drives the research of clean-efficient-sustainable alternative energy sources. Solar thermal power is regarded as a potential clean energy but owns disadvantages of instability and intermittency, hence achieving efficient storage to ensure sustainable supply of the thermal energy is the key of solar thermal power generation technology. Distributed solar thermal power system is a promising clean energy supply for low carbon cities. Thermal energy storage is one of the key technologies for meeting the global energy challenge, widely applied to CSP systems, industrial waste heat recovery and peak regulation of urban power grid. Metal oxides redox system is considered as a promising concept for thermochemical heat storage, based on reversible conversions of different valence states. Air acts both as reactive material and heat transfer fluid, leading to cost effective and simplified systems. Mn_2O_3/Mn_3O_4 redox system is one of the most attractive for thermochemical storage because of its low cost and suitable reaction temperature range (800°C-1000°C). Agrafiotis[1] found that Mn_2O_3 was reduced to Mn_3O_4 at temperature ranging of 900°C to 920°C and was hardly oxidized in reverse. Carrillo[2] studied on the factors of the poor re-oxidation performance and found that the reaction rate of oxidation has great relations with morphology features of Mn_2O_3. Agrafiotis[3] reported that the addition of Fe_2O_3 can raise the oxidation rate. But the reaction conversion of the materials declined with cycle going on. Current research about Mn-Fe mixed oxides is insufficient, further research is needed. This work investigated the mechanism of Fe addition to Manganese oxides and the reaction characteristics of Mn-Fe mixed oxides.

2. PAPER STRUCTURE

2.1 Experimental setup and methodology

The Mn_2O_3 mixed with 10, 20, 30, 40 mol% Fe_2O_3 were synthesized by citrate sol-gel method. The materials were identified by XRD (X-Pert, PANalytical B.V.) and field emission scanning electron microscopy (FESEM, SIRON, FEI). Fig 1 shows the XRD spectra, Manganese oxide bixbyite and Iron oxide spinel were detected in the materials. The intensity of Iron oxide spinel characteristic peak is enhanced gradually with the increase of Fe proportions. The TGA was performed in a HITACHI STA 7200. A Netszch STA 449 Jupiter F3 instrument was employed for DSC. All measurements were performed under synthesis air mixture of 20% oxygen and 80% nitrogen with a 50mL min^{-1} gas flow. The materials were extruded into honeycombs with porous structure for further investigation. The honeycombs are put into an alundum tube, used as the reaction vessel. Thermocouple points are tied to the wall of the honeycomb holes to measure the temperature of the honeycombs. The alundum tube is heated by furnace capable of reaching 1200℃ with 10℃/min maximum heating/cooling rate. Air is used as the reaction gas provided by air compressor. The air passes an Omega mass flowmeter to ensure the flow of air maintaining at constant of 10L/min before entering the alundum tube. The exit is divided into two ways, one directly discharges the gas to atmosphere and another is connected to a
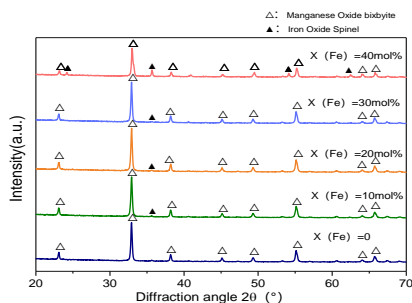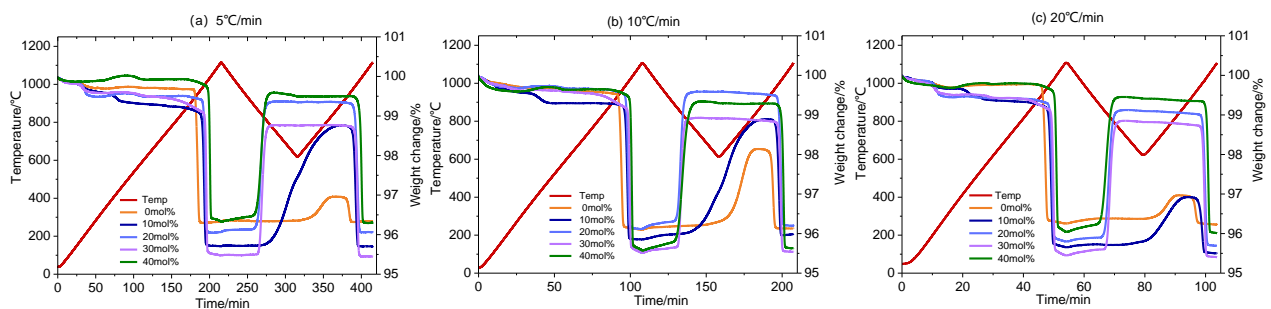
Signal paramagnetic oxygen analyzer to record the oxygen concentration variation.

2.2 Result and discussion

2.2.1 The mechanism of Fe addition

Fig 2 shows the TGA curves of the powders of different doping ratio under the heating/cooling rate of 5, 10, 20℃/min at the condition mentioned above. For reduction process, all the weight-loss ratios of the powders were approximately 3.38%, equal to the theoretical value of pure Mn_2O_3. However, if the Fe addition act as inert material, the theoretical value of doping materials should be equal to the 3.38% multiplying the percentage of Manganese oxide. The result demonstrates that iron oxide participates in the reaction instead of presence as an inert material. Fe_2O_3 decomposes at 1392℃ well above the temperature in this work. Hence the Fe addition joins the reaction not in a form of single iron oxide. The powders' performances at oxidation process appeared obvious differences. Only a little fraction of pure Mn_2O_3 was oxidized. The oxidation of the $(Mn_{0.9}Fe_{0.1})_2O_3$ was improved than pure Mn_2O_3, but it was also a certain extent to full oxidation. It was worth mentioning that powders that Fe proportion of 20%mol, 30%mol and 40%mol regained the lost weight almost entirely during the cooling stage within a short time. All three powders reacted completely reversibly without distinction, exhibiting well reaction characteristics. Taking the best-performed $(Mn_{0.8}Fe_{0.2})_2O_3$ under ramp rate of 10℃/min for example to analyze the reaction process of the material. During the first heating period, the reactant decomposed with heat absorption when the temperature reached 978℃. The reduction process continued for 4 min and ended at 1023℃. Fast endothermal reaction rates shorten the charge process, crucial for the application in CSP thermochemical storage. During the cooling period,

Fig 1 XRD diagram of the materials

Fig 2 TGA curves comparison of the materials at different ramp rate

reduction product was oxidized back with heat release when temperature was cooled to 878℃. The oxidation process was relatively slow than the reduction process with duration of 9 min and ended at 784 ℃. The difference of reaction initial temperature between reduction and oxidation was 100℃. Materials with Fe addition of 20mol%, 30mol% and 40mol% accomplished the redox process in a short time during the heating and cooling process, illustrating the advantages of fast reaction rate and good stability brought from the addition of Fe.

The Mn-Fe-O phase diagram[4] is shown in Fig 3(a), the pure Mn_2O_3 presents two phases of bixbyite and tetragonal spinel with a critical temperature around 880℃ in whole process. The Mn-Fe mixed oxides will go through a two-phase zone (T-spinel and Bixbyite, T-Spinel and C-Spinel) in reaction when the addition of Fe is between 5%mol and 15%mol, possibly accounting for the bad reversibility of pure Mn_2O_3 and $(Mn_{0.9}Fe_{0.1})_2O_3$ in oxidation. However, the materials convert from bixbyite structure to cubic spinel structure directly when the addition of Fe is between 20 mol% and 40 mol%. Fig 3(b-d) shows the contrast of actual weight loss/gain rate of the materials with different addition of Fe. For reduction process, the mass loss rates of all the materials are in good agreement of theoretical values. But in oxidation

comparison to pure Mn_2O_3/Mn_3O_4 redox system. To study the mechanism of the Fe addition to the Mn_2O_3/Mn_3O_4 redox system. The phase analysis of reduction process is carried out firstly. Fig 4 shows the XRD results of reduction products. The pure material is transformed into hausmannite from bixbyite. However, the intensity of hausmannite (tetragonal spinel) is weakened gradually and jacobsite (cubic spinel) is formed with the increase of Fe addition, according with the analysis in Fig 3(a). The characteristic peak of jacobsite is particularly obvious in $(Mn_{0.6}Fe_{0.4})_2O_3$. The cations are approximately normal distribution in the crystal structure of $MnFe_2O_4$. Mn ions and Fe ions occupy the A-site and B-site commonly. 80% of the Mn ions take up the A-site and appears divalent. The rest of A-site is occupied by Fe ions. Both Mn ions and Fe ions in $MnFe_2O_4$ appear divalent and trivalent, illustrating the addition of Fe declines the temperature at which Fe^{3+} is reduced to Fe^{2+}, part of Fe^{3+} in materials are reduced to Fe^{2+} in the reduction process. Hence the crystal structure transformations of the Mn-Fe mixed oxides reduction might have two steps. Firstly, bixbyite is reduced to hausmannite at high temperature calcination. Then hausmannite and iron oxide spinel form into jacobsite ($MnFe_2O_4$) with the temperature gradually increased. In contrast, the oxidation process consists of two parts, $MnFe_2O_4$ is oxidized to Mn_2O_3 and Fe_2O_3, and Mn_3O_4
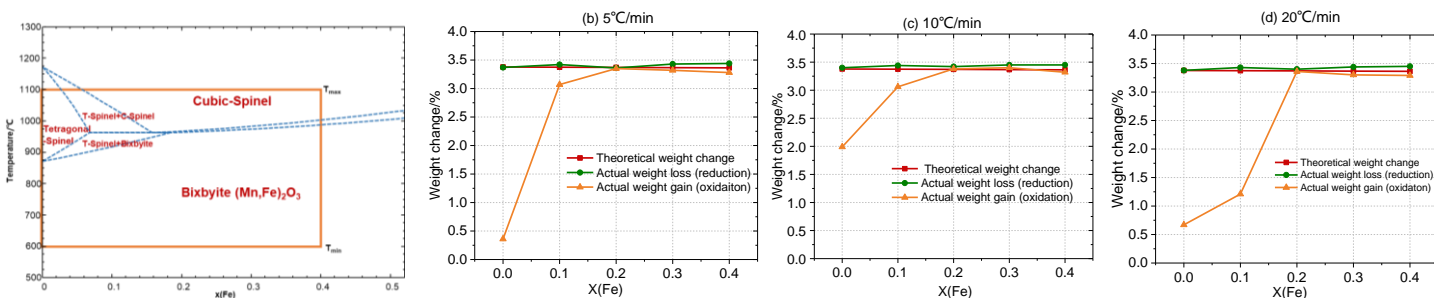

Fig 3 (a) Fe-Mn-O_2 phase diagram at pO_2=0.20 atm, (b-d) The contrast of actual weight increase rate and weight lose rate

process, the pure Mn_2O_3 and $(Mn_{0.9}Fe_{0.1})_2O_3$ are unable to regain the mass completely, The oxidation ratios of $(Mn_{0.9}Fe_{0.1})_2O_3$ is respectively 88%, 88% and 33% at ramp rate of 5, 10, 20℃/min. At low Fe addition, it seems that the presence of tetragonal-spinel may have negative effects on the oxidation reaction, resulting in the bad reversibility. However, the reversibility of Mn_2O_3/Mn_3O_4 is significantly enhanced with the addition of Fe beyond 20mol%. The actual weight loss/gain rates of the materials with Fe addition of 20mol%, 30 mol% and 40 mol% at each ramp rate are close to the theoretical value. These materials are almost completely re-oxidized in
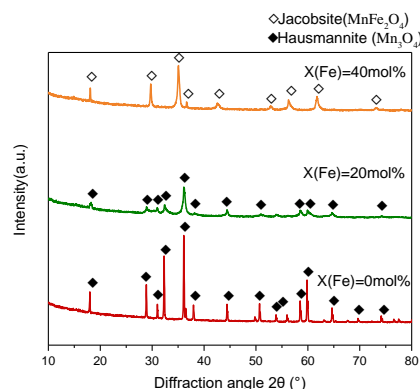

Fig 4 Phase analysis of reduction products

converts to Mn_2O_3. The hypothesis should be confirmed via more experimental methods. The addition of Fe above 20mol% helps to the Mn_2O_3 away from two-phase zones, leading to an enhancement to the oxidation conversion. $(Mn_{0.8}Fe_{0.2})_2O_3$ is regarded as the optimal components via comprehensive considerations including reaction rate, reaction mass change fraction and starting temperature difference between reduction and oxidation, hence the following research will focus on it.

2.2.2 The reaction characteristics of $(Mn_{0.8}Fe_{0.2})_2O_3$

In reduction process, oxygen is released with the reaction continuing, leading to the increase of oxygen concentration in system. Rapid reaction rate will cause the accumulation of oxygen especially in large-scale storage system. The excessive oxygen concentration will restrain the reaction itself. However, oxygen is absorbed in oxidation process. Higher oxygen concentration makes for the combination of oxygen and material, promoting the reaction conversion. Hence it is vital to study the influences of the oxygen partial pressure on the reaction. Materials of $(Mn_{0.8}Fe_{0.2})_2O_3$ are test via TGA under the oxygen proportion of 30%, 40%, 50%, 60%, 70%, other parameters stay the same as before. the TGA curves are shown in Fig 5(a). It is obviously that the materials have good reaction performance in each oxygen proportion. The weight loss/gain ratios accord with the theoretical value, presenting well reversibility. Fig 5(b) shows the time reaction needed at each oxygen proportion. The oxygen proportion variation has hardly influences on reduction process. Material at each oxygen concentration starts and ends almost at the same time, illustrating that material of $(Mn_{0.8}Fe_{0.2})_2O_3$ can overcome the inhibiting effect of the high oxygen concentration in reduction process. It is crucial in actual application because quantities thermal storage materials release large amount of oxygen in a short time. For oxidation process, the reaction time decreases with the increase of oxygen proportion, according with the theoretical analysis mentioned above. The conversion temperature

curves at each oxygen proportions are shown in Fig.5(c) and Fig.5(d). Both reduction curve and oxidation curve shift to high temperature area with the increase of oxygen proportion. The reduction conversion declines and oxidation conversion increases at the same temperature with the oxygen proportion increase. The starting temperature of reduction and oxidation is also influenced by oxygen partial pressure. The starting temperature of reduction increases from 987 ℃ to 1015 ℃ and the starting temperature of oxidation increases from 871 ℃ to 955 ℃. The oxidation temperature integrally shifts to higher temperature region, indicating that thermal hysteresis is weakened with the enhancement of oxygen concentration, making for the promotion of the heat utilization quality of the materials. However, the increase of reduction temperature is undesirable, hence the oxygen released via reduction process needs to be discharged in time to facilitate the proceeding of the reduction in practical application. High oxygen partial pressure is available for the promotion of the oxidation reaction rate, which obeys Le Chatelier principle. From the analysis of the results given above, the fluctuation of oxygen concentration has little influences on the performance of reaction, giving more possible applications in more complex atmosphere.

The materials exhibited good cyclic stability after 10 cycles, shown in Fig 6. The enthalpy of $(Mn_{0.8}Fe_{0.2})_2O_3$ was measured by DSC under synthetic air, shown in Fig 7. The endothermic peak and exothermic peak are observed distinctly, corresponding to reduction and oxidation respectively. The enthalpy value of reduction is 171.95 J/g, and the enthalpy value of oxidation is 201.56J/g. The oxidation one is slightly higher than the reduction one, it might be cause by the instrument fluctuation error. The oxidation enthalpy is usually regarded as the energy storage density of the material. The value is almost equal to the value of 202 J/g of pure Mn_2O_3, illustrating that the
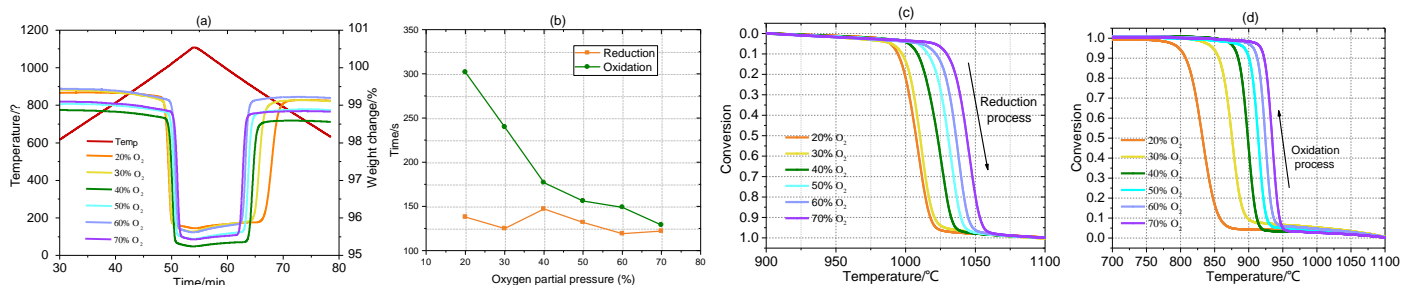

Fig 5 Conversion temperature curves at each oxygen proportions

addition of Fe has no impact on the energy storage density of the material.
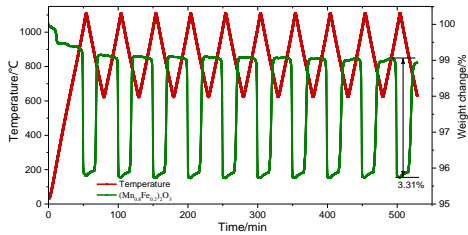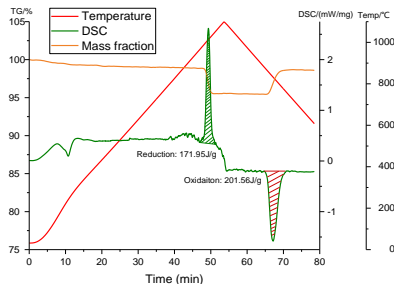

Fig 6 Cyclic TGA curve of $(Mn_{0.8}Fe_{0.2})_2O_3$

Fig 7 Heat flow curve of $(Mn_{0.8}Fe_{0.2})_2O_3$

2.2.3 *reaction performance of extruded honeycombs*

Due to the sintering of particles at high temperature in large-scale energy storage systems, the materials are preferred to be manufactured into honeycomb or foam structure for application. The ordered porous in honeycombs lowers the flow resistances of reaction gas and increases surface contact area, enhancing the heat transfer between the materials and reaction gas. Fig 8 presents the schematic diagram of experimental setup.
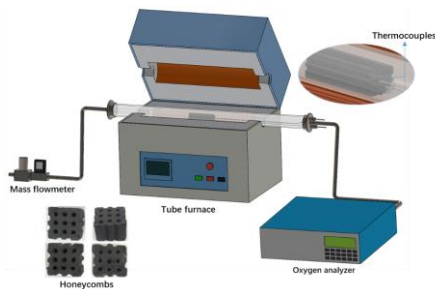

Fig 8 Schematic diagram of experimental setup

Four honeycombs totally approximately 110g are used in the preliminary experiment to study the reaction characteristics of huge amount materials compared to that of tiny amount in TGA measurements. The honeycombs were heated from indoor temperature to 1100℃ firstly staying for 90 minutes and then cooled

down to 700℃ maintaining for 90 minutes in keeping with the temperature in TGA tests The oxygen concentration and temperature variation curves are shown in Fig 9, in reduction process, the materials were decomposed with oxygen released, whose concentration increased rapidly until reached peak value, then decreased until reached normal value in air atmosphere. The temperature of honeycombs increased until the start of reduction, then maintained 990 ℃ for 10 minutes while the alundum tube wall is at 1100 ℃, forming a temperature gap between honeycombs and wall of alundum tube, after finishing the reduction, the honeycombs were gradually heated to 1088℃ with 12℃ heat transfer difference between honeycombs and alundum tube wall. After constant temperature stage, the oxidation took place when the temperature of honeycombs was cooled down to 850℃. The exothermic reaction released the heat rapidly, resulting in that honeycombs kept the temperature until the reaction termination regardless of the temperature difference between the wall. above, the temperature gap between the reduction and oxidation leads to the loss of heat grade, trying to enhance the reaction temperature of oxidation is essential to promote the heat grade of the materials. Future experiments with doping other materials to adjust the reaction temperature region are scheduled to investigate this issue.
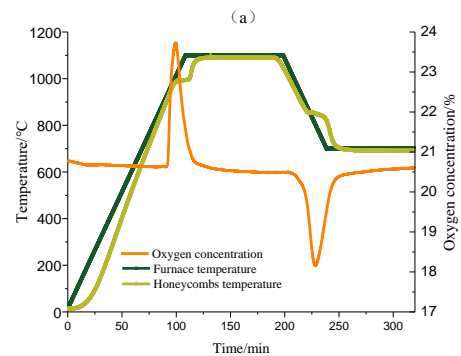

Fig 9 oxygen concentration and temperature

The cyclic stability of extruded honeycombs needs to be examined under more cycles. Therefore, the other four honeycombs weighted total 88.64g were used for the test of cycling stability. The honeycombs were totally examined for 100 cycles, shown in Fig 10. The oxygen concentration curves were integrated for the calculation of oxygen volume, which could be transferred into the mass of materials participated in the reaction equivalently with multiplying relevant parameters. The

effective mass is divided by total mass to acquire the ratio of reaction. The ratio takes on rising trend in first fifteen times and approaches to 98% at the eighth. It is speculated that the rising trend is caused by the volume expansion, resulted from the transference of oxygen in initial several cycles. Then the ratio is stabilized at 85% until the last cycle. The average reaction ratio of oxidation is 87.9%, as a consequence, the average effective enthalpy of oxidation is 177.17J/g. The results illustrate that the extruded honeycombs exhibit good sustainable cyclic stability.

Thermochemical energy storage with redox metal oxides is promising for high temperature and highly efficient thermal energy storage. The addition of Fe in Mn_2O_3 by sol-gel method has improved the shortcomings of low re-oxidation degree and slow oxidation rate of Mn_2O_3/Mn_3O_4 system. The reasons for the improvement of the reaction properties and the influencing factors of the reaction process are explained as the presence of $MnFe_2O_4$. $(Mn_{0.8}Fe_{0.2})_2O_3$ is regarded as the optimal components via comprehensive considerations. Extruded honeycomb materials present good reaction performance and potentials for large-scale energy
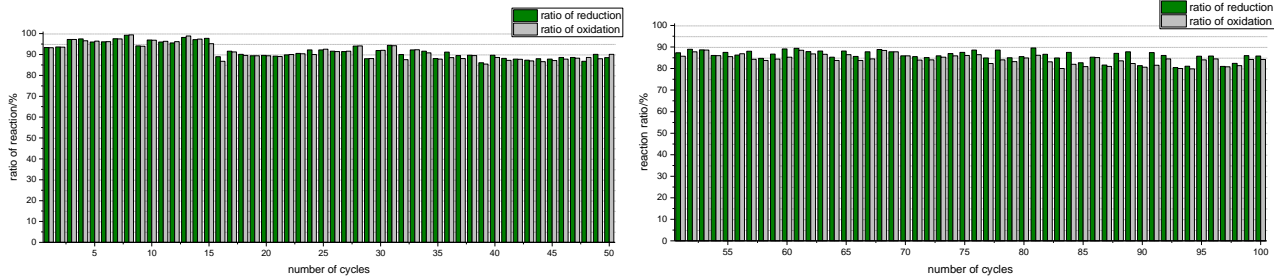

Fig 10 reaction ratios of 100 cycles

In microscopic perspective, apparent morphologies of the materials sampled before reaction and at 30th cycle, 70th cycle and 100th cycle via SEM are shown in Fig 11. The growth of the crystal is distinct. The materials exhibited flocculent structures before reaction, then the growth of nuclei began, flocculent crystal was gradually coarsening with the increase of cycle number, the obvious angular arose after 30 cycles. Crevice was found after 70 cycles. The results show that sintering has little impacts on the reaction performance.

storage application in CSP. More experimental research for lab-scale and large-scale energy storage systems need to be done in future.

REFERENCE

[1] Agrafiotis, C., M. Roeb and C. Sattler. Exploitation of thermochemical cycles based on solid oxide redox systems for thermochemical storage of solar heat. Part 4: Screening of oxides for use in cascaded thermochemical storage concepts. Solar Energy, 2016. 139: p. 695-710.
[2] Carrillo A J, Serrano D P, Pizarro P, et al. Thermochemical heat storage based on the Mn_2O_3/Mn_3O_4 redox couple: influence of the initial particle size on the morphological evolution and cyclability[J]. Journal of Materials Chemistry A, 2014, 2.
[3] Agrafiotis C,Block T, Senholdt M, et al. Exploitation of thermochemical cycles based on solid oxide redox systems for thermochemical storage of solar heat. Part6: Testing of Mn-based combined oxides and porous structures[J]. Solar Energy, 2017, 149:227-244.
[4] André, L., S. Abanades and L. Cassayre. High-temperature thermochemical energy storage based on redox reactions using Co-Fe and Mn-Fe mixed metal oxides. Journal of Solid State Chemistry, 2017. 253: p. 6-14.
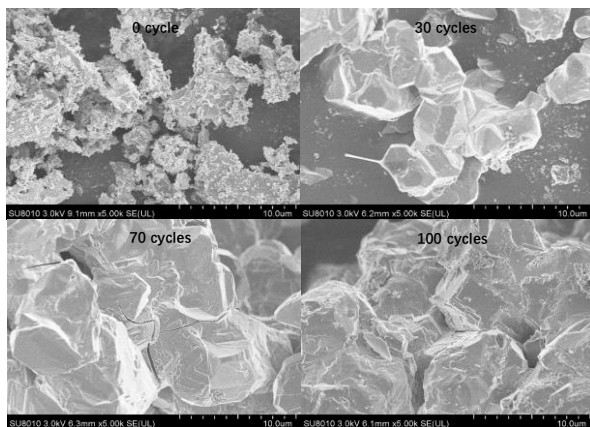
Fig 11 Apparent morphology at different cycles

2.3 Conclusions