

Article

Comparative Study of Heat-Discharging Kinetics of Fe-Substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ Being Subjected to Long-Term Cycling for Thermochemical Energy Storage

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Abstract: The heat-discharging kinetics of an iron-substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ redox pair subjected to long-term thermal cycling tests using a temperature swing process at high temperatures was investigated for next-generation concentrated solar power plants equipped with thermochemical energy storage. The heat-discharge mode kinetics for long-term thermal-cycled samples have never been reported. Additionally, comparisons of the heat-discharge mode kinetics for both long-term thermal-cycled and as-prepared samples have never been discussed. In terms of the reproducibility and sustainability of thermochemical energy storage, kinetic evaluations of samples with thermally stable morphologies subjected to long-term thermal cycling at high temperatures are important for next-generation solar thermal power plants. For the long-term thermal-cycled sample, the A2 model based on the Avrami–Erofeev reaction describes the discharging mode behavior in a fractional conversion range of 0–0.24, the contracting area (R2) model best fits in a fractional conversion range of 0.24–0.50, and the third-order (F3) model matches in a fractional conversion range of 0.50–0.70. For the as-prepared sample, the power-law (P2) model describes the behavior of the first part of the discharging mode, whereas the Avrami–Erofeev (A4) model best fits the last half of the discharging mode. The predicted theoretical models for both samples were compared with previous kinetic data.

Keywords: kinetic analysis; iron-substituted manganese oxides; thermochemical storage; next-generation concentrated solar power; long-term thermal cycling; heat-discharging



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1. Introduction

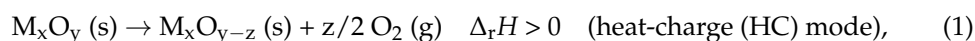
Renewable energy sources represented a record share (an estimated 29%) of the global electricity mix in 2020 due to their low operating costs and preferential access to electricity networks during periods of low electricity demand [1]. According to the Renewables 2021 Global Status Report [2], as of 2019, modern renewable energy, eliminating the traditional biomass use, ranked an estimated 11.2% of the total final energy consumption (TFEC), followed by renewable heat (4.2% of TFEC) and biofuels for transport (1.0% of TFEC), which is an increase of 2.5% in comparison with 2009.

Concentrated solar thermal systems convert solar radiation in the form of heat, which can be utilized for various industrial and chemical processes, including well-established power generation (concentrated solar power, CSP) and promising thermochemical processes, to produce green hydrogen and synthetic gas. CSP plants are a promising alternative technology to sustainably generate electricity in countries located in regions with high solar radiation [3]. High-temperature thermal storage technologies contribute to improving CSP plant efficiency and overcoming the gap between peak solar and peak demand hours because their integration may solve the problem of the intermittency associated with solar energy to allow for uninterrupted electricity production [4,5]. The percentage of CSP plants with thermal energy storage (TES) as of 2020 was approximately 70% of the total installed

capacity [6], where various TES technologies, including molten-salt, concrete, and steam, are used for storage capacity in commercial CSP plants. Alternatively, in noncommercial TES technologies, latent thermal storage using phase-change materials, thermochemical storage, particulate solids, and liquid metals are still being researched.

Thermal energy can be stored using three different concepts, namely, sensible, latent, and thermochemical TES [7–9]. This study focuses on thermochemical TES, which can absorb, store, and release heat via a reversible redox reaction. Thermochemical TES is one of the efficient methods with the potential for higher energy efficiency to store chemical and thermal energy, as compared with sensible and latent TES technologies. The most relevant redox reactions for thermochemical TES in CSP are solid-gas reactions including the calcium carbonate/decarbonate process [10–15], ammonia synthesis–decomposition [16–19], metal/metal oxide [20], hydroxides [21,22], and metal oxide redox processes [23]. Among the thermochemical TES methods, solid-gas reactions involving calcium looping and metal oxide redox processes have attracted considerable attention for integration into next-generation CSP plants that develop its system in the world.

The metal oxide process using the reversible redox chemical reaction using a metal oxide is generally written as:



The high-temperature heat provided by concentrated solar radiation drives the endothermic HC mode to chemically charge (store) it as a reaction product of M_xO_{y-z} in the reduced form (Equation (1)). The solid-product M_xO_{y-z} can be stored in the storage bin (tank) of the CSP plant, which may solve the intermittency problem associated with solar energy to allow uninterrupted electricity production. The following exothermic HD mode discharges (releases) the stored heat through the oxidation of M_xO_{y-z} by a gas stream containing oxygen (Equation (2)). Consequently, the reduced form of M_xO_{y-z} returns to the oxidized form of M_xO_y , enabling the consecutive implementation of Equations (1) and (2) [24].

In the United States, the Generation-three CSP system (Gen3 CSP) phase-three project for a next-generation commercial CSP plant to operate at temperatures $>700^\circ\text{C}$ is in progress [25,26]. A project of the Gen-three Particle Pilot Plant selected a falling-particle receiver system that utilizes a moving solid particulate as the heat transfer fluid (HTF) and storage media [27]. An open-type volumetric receiver [28,29] was designed, manufactured, and tested in the EU, which allows for the use of air stream as the HTF and metal oxide as the thermochemical storage medium. Additionally, a next-generation CSP project was implemented during 2016–2020 to develop key HTF technologies that can be used for the implementation of direct TES, high-temperature receivers, and a fluidized particle-in-tube concept allowing high-efficiency new cycles $>50\%$ [30,31]. In Australia, a liquid sodium [32] or molten-salt [33] receiver in the central tower system was investigated as a third-generation CSP operating at temperatures greater than the existing external molten nitrate salt receivers. Although thermochemical TES was not implemented owing to the technological complexity of industrial applications, it is currently in the research and development stages.

The essential characteristics of thermochemical TES using metal-oxide redox reactions in next-generation CSP applications are thermodynamics, operating temperature, thermal storage capacity/density, material costs, kinetics of reversible reactions, cyclical feasibility, toxicity to humans, and environmental safety. BaO_2/BaO [34–36], Co_3O_4/CoO [37–47], Mn_2O_3/Mn_3O_4 [44,48–53], Fe_2O_3/Fe_3O_4 [54], CuO/Cu_2O [55], and perovskite oxide systems [56–65] have been investigated from the viewpoints of thermodynamics, kinetic analysis, thermal durability, and heat exchanger/reactors. Among the thermochemical TES materials, the manganese-iron oxide ($(Mn, Fe)_2O_3/(Mn, Fe)_3O_4$) system, in which

some of the manganese ions are replaced with foreign iron ions to overcome the disadvantages of the $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ system (poor TES capacity/density, slow kinetics of HD mode, and large hysteresis loop), has been examined, evaluated, and tested as a promising thermochemical TES material.

Several researchers have studied the kinetics of iron-substituted Mn_2O_3 . Kinetic equations, the influence of iron substitution, chemical energy storage density, repeatability, and reactivity over 100 cycles for the HC mode of iron-substituted Mn_2O_3 , as compared with the non-substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ system, have been reported in the literature [66–72]. In contrast, several investigations have kinetically analyzed the HD mode of non-substituted and iron-substituted manganese oxides [66,67,73,74]. Gillot et al. first reported the oxidation kinetic behavior of a non-substituted Mn_3O_4 system using thermogravimetric analysis (TGA). The authors tested and evaluated the samples under isothermal oxidation at different temperatures ($T = 162\text{--}290\text{ }^\circ\text{C}$ in a constant O_2 atmosphere, $P_{\text{O}_2} = 100\text{ kPa}$) [73]. Carrillo et al. studied the oxidation kinetics of a thermally reduced sample in which 20% iron-substituted Mn_2O_3 was first subjected to the HC mode up to $1000\text{ }^\circ\text{C}$ under an argon atmosphere. The sample was kinetically evaluated using isothermal oxidation at different temperatures ($T = 650\text{--}800\text{ }^\circ\text{C}$) under an air flow [66]. Woken et al. kinetically investigated a granular sample of 25% iron-substituted Mn_2O_3 using TGA. An oxidation kinetic formula that considers the influence of P_{O_2} was derived from isothermal measurements [67]. Al-Shankiti et al. studied the oxidation kinetics of iron manganese oxide spinel (MnFe_2O_4) (intensive mixing of $\text{Fe}_2\text{O}_3:\text{Mn}_2\text{O}_3 = 2:1$ composition) using TGA. To acquire the kinetic data of the HD mode, the thermally reduced sample under a N_2 atmosphere was subjected to an air stream at different heating rates ($2.5\text{--}10\text{ K/min}$) in a TGA device [74]. To the best of our knowledge, there are limited evaluations regarding the kinetic analysis of the HD mode of the emerging iron-substituted Mn_2O_3 with a thermally stable morphology subjected to long-term thermochemical cycling of redox reactions at high temperatures. Additionally, a comparison of the kinetics of the HD mode for long-term thermal-cycled and as-prepared samples has never been reported and discussed in previous studies.

The present authors investigated and compared the thermochemical TES performances (initiation/termination temperature of the redox reaction, storage density/capacity, repeatability, and HC/HD behavior) of manganese oxides with various iron substitution levels using TGA and differential scanning calorimetry at a laboratory scale [53]. The 20 mol% iron-substituted Mn_2O_3 exhibited excellent repeatability of the redox cycle without degradation of the oxidation profile during the HD mode, a high TES capacity/density, and a small hysteresis loop, as compared with the non-substituted sample. In a previous study, the present authors examined the long-term thermal cycling of a powder-like sample and reported that long-term thermal cycling causes a morphological change in the sample due to sintering/coagulation of fine particles at high temperatures, as compared with that in the as-prepared sample, which affects the HC kinetics with oxygen release. This causes variations in the reaction mechanism, Arrhenius parameters, and reaction model, leading to variations in the HC kinetic equation during the HC mode [72]. The HC kinetic formula was estimated under non-isothermal conditions using a particle-connected porous sample generated using a long-term thermal cycling process.

In this study, the HD mode for a sample subjected to long-term thermal cycling at high temperatures under a constant oxygen partial pressure was kinetically analyzed and compared with that of an as-prepared sample. The HD kinetics were conducted under non-isothermal conditions, and the experimental data showed that the sample was cooled at $1050\text{--}650\text{ }^\circ\text{C}$ at different cooling rates of $3\text{--}7\text{ K/min}$. The morphologies and elemental distributions of the long-term thermal-cycled and as-prepared samples were compared. The kinetic data of the HD were compared with those of the HC obtained from the long-term thermal-cycled sample. Finally, a comparison of the HD kinetics in this investigation was discussed with the previous kinetic results reported under various test conditions.

2. Experimental Procedure

2.1. Synthesis and Characterization of Iron-Substituted Mn_2O_3

Iron-substituted Mn_2O_3 was prepared using manganese (II) and iron (III) nitrates using a modified Pechini process [53]. Briefly, stoichiometric quantities of the nitrate reagent, ethylene glycol, and citric acid were dissolved in deionized distilled water. The aqueous solution was stirred and heated at 80 °C for 1 h in an oil bath for mixing. Subsequently, the solution was heated at 170 °C for 0.5 h for gel formation. The gel was dried at 180 °C for 4.5 h and crushed in an agate mortar. The powder-like precursor was heated at 900 °C for 8 h under an air atmosphere in an electric oven.

The powder-like samples synthesized in this study were characterized by X-ray diffraction with $Cu K_{\alpha}$ radiation (XRD; D2Phaser, Bruker, MA, USA). The measurement conditions were described in the previous paper [72].

The morphology and particle size were observed and evaluated using scanning electron microscopy equipped with an energy-dispersive X-ray spectrometer (SEM; JCM-6000, JEOL, Tokyo, Japan) (EDS, relative error of <1%). The observation conditions were at an acceleration voltage (15 kV), beam current (200 mA), beam size (1 μm), step size (0.5 μm), and sampling time (0.1 s). To enhance the conductivity and avoid charge build-up, a pretreatment process of gold evaporation was conducted before SEM observation.

2.2. Long-Term Thermal Cycling

The experimental setup for the long-term thermal cycling of consecutive HC and HD modes was performed in a TGA reactor (STA2500 Regulus, NETZSCH, Selb, Germany; weight resolution (0.03 μg), temperature resolution (0.3 K)) equipped with a differential thermal analyzer (DTA) with a type-S thermocouple (temperature resolution ($\pm 0.0025 \times |t|$ °C)). The detailed methods and conditions of thermal cycling test were explained in the paper [72].

2.3. Non-Isothermal Kinetic Analysis of HD Mode

A kinetic analysis of the non-isothermal HD mode for the test samples was conducted, evaluated, and compared using a TGA reactor using the same method. The sample was preheated to 800 °C for 2 h to remove the adsorptive gas species and volatiles on the surface of the sample. Subsequently, to conduct the HC mode, the sample was heated to 1050 °C at 20 K/min and flowed through a gas stream at a flow rate of 250 cm^3/min^{-1} at a standard state. Subsequently, the test sample was cooled from 1050 to 650 °C at cooling rates of 3–7 K/min to acquire the kinetic data of the non-isothermal HD mode. The kinetics of the HD mode were analyzed using non-isothermal master plots for various cooling rates ($\frac{dT}{dt}$).

The fractional conversion of α in the sample was measured and recorded during the HD mode as follows:

$$\alpha = \frac{\Delta m_{HD}(t)}{\Delta m_{HC}} \quad (3)$$

where Δm_{HC} is the total mass decrease during the HC mode and $\Delta m_{HD}(t)$ is the integrated mass increase at time t during the HD mode.

Isoconversion was used to estimate the Arrhenius parameters for the HD mode involving O_2 absorption from the time-course data [69].

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) = k(T)f(\alpha), \quad (4)$$

where A and E_a are the pre-exponential factor and apparent activation energy for the HD mode, respectively; R is the gas constant; $k(T)$ is the rate parameter as a function of temperature T ; and $f(\alpha)$ is a theoretical model function of α , which represents the reaction mechanism.

The generalized time (θ) is expressed as:

$$\theta = \int_0^t \exp\left(-\frac{E_a}{RT}\right) \cdot dt. \quad (5)$$

Different cooling rates were applied in the non-isothermal kinetic analysis of the HD mode. Thus, the diagram of the non-isothermal master plots corresponds to

$$\frac{d\theta}{dt} = \exp\left(-\frac{E_a}{RT}\right), \quad (6)$$

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{f(\alpha)}{f(\alpha)_{\alpha=0.5}}, \quad (7)$$

where $f(\alpha)_{\alpha=0.5}$ is a series of data plots at $\alpha = 0.5$, which corresponds to the control point of the data fitting. The experimental values plotted against α were compared with various theoretical models for the HD mode with decreasing temperatures to identify an appropriate theoretical model.

The differential isoconversion methods [75] were used for determining the apparent Arrhenius parameters:

$$\ln \frac{d\alpha}{dt} = \ln[A \cdot f(\alpha)] - \frac{E_a}{RT}. \quad (8)$$

The sample temperature (T) can be related to various reaction times (t) and cooling rates (β):

$$T = T_0 + \beta t, \beta = \frac{dT}{dt} \quad (9)$$

where T_0 is the initiation temperature of the HD mode (1050 °C). Equation (4) is written in terms of the cooling rate (β) as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha). \quad (10)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT = \left[\frac{AE_a}{\beta R} p(x) \right]_{T_0}^T \quad (11)$$

$$p(x) = \frac{\exp(-x)}{x(x+2)}, x = \frac{E_a}{RT}, \quad (12)$$

where $p(x)$ is a first-order rational approximation for the term $x \gg 15$ as a function of the Schlömilch series expansion [76]. Thus, the variations in the fractional conversion based on the model prediction were compared with those based on the experimental results.

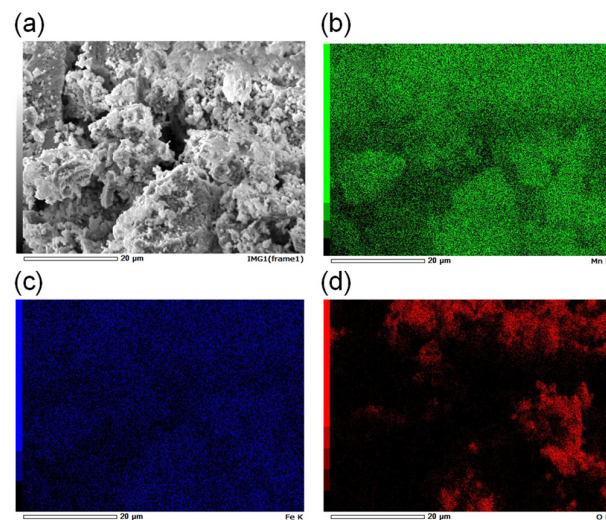
3. Results

3.1. Comparison of the Morphologies and Element Distributions of the Long-Term Thermal-Cycled and As-Prepared Samples

In this section, the morphologies and element distributions of the long-term thermal-cycled sample are first compared with those of the as-prepared sample to evaluate the impact of long-term cyclic testing in terms of histological features. Figure 1 shows a secondary electron image (SEI) micrograph and mapping images of the constituent elements (manganese, iron, and oxygen) for (a–d) the as-prepared and (e–h) the long-term thermal-cycled samples. Irregularly shaped small particles <1 μm in size and plate-like aggregations of particles 1–50 μm in size were observed in the SEI micrograph of the as-prepared sample (Figure 1a). Additionally, numerous pores were observed in the aggregates. The SEI micrograph shows that the aggregation of pores occurred because of the calcination of the gel formed during the Pechini process or the sintering of small particles during the drying or calcination stage. In the Pechini process, metallic ion species and citric acid form chelate

compounds in an aqueous solution, and the resulting compound reacts with polyalcohol (ethylene glycol) to produce a gel-like precursor in which the constituent ionic species are homogeneously distributed by esterification. Finally, the precursor was calcined at high temperature to produce ceramic composite particles with a homogeneous mixture without segregation of the constituent ions (iron-substituted manganese oxide). Aggregation may result from the gel-like precursor or from the sintering of the particles at high temperatures during the calcination stage.

As-prepared sample



Long-term thermal-cycled sample

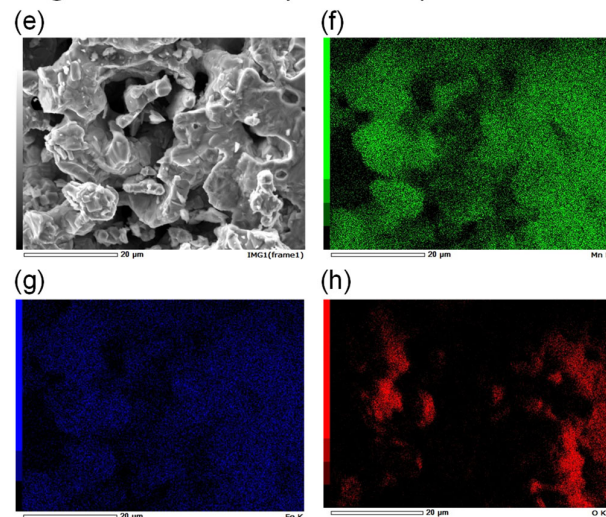


Figure 1. (a) SEI image and EDS mapping of (b) manganese, (c) iron, and (d) oxygen of the as-prepared sample. (e) SEI image and EDS mapping of (f) manganese, (g) iron, and (h) oxygen of the sample which was subjected to the thermal-cycling test.

As described above, the characteristics of the Pechini process include obtaining ceramic composite particles in which metallic ions are homogeneously distributed. To examine the microscopic distribution of the constituent elements in the as-prepared sample, EDS mapping of each constituent element was performed and compared with that of the SEI micrograph. In the manganese mapping image (Figure 1b), the green region is widely distributed in the morphology of the aggregation in the SEI image. In the iron mapping image (Figure 1c), the pattern of the blue region almost overlaps with that of manganese. The oxygen mapping image (Figure 1d) shows a weaker intensity than those of manganese

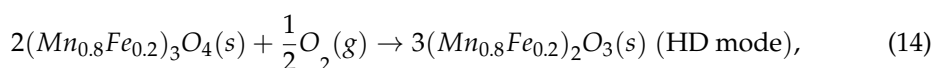
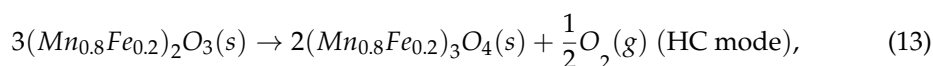
and iron in the EDS analysis at an accelerating voltage (15 kV) because oxygen is a light element. The pattern of the red region is similar to that of the green and blue regions. These results indicate that the aggregation in the SEI image corresponds to a manganese-iron oxide, which is homogeneously distributed without element segregation.

The SEI micrograph (Figure 1e) of the sample after long-term thermal cycling, as compared with the as-prepared sample, shows that spherical aggregates were observed, and the aggregates coarsened and connected, resembling the three-dimensional shape of a porous material. Additionally, many small particles fused on the aggregates, and a step-like morphology appeared on the surface of the aggregates. The SEI micrograph indicates that the initial aggregation and small particles in the as-prepared sample caused secondary aggregation at high temperatures during the long-term thermal cycling tests. Notably, the secondary aggregation that formed after the long-term thermal cycling test was not a dense and non-porous configuration. This configuration may be related to the conductivity of the gas stream involving oxygen during the HD mode, in which the oxygen-released sample reacts with oxygen, leading to the HD kinetics of the sample.

The microscopic distribution of the constituent elements was observed in the long-term thermal-cycled samples. The manganese and iron mapping images (Figure 1f,g, respectively) correspond to the SEI micrograph. As in the as-prepared sample, the manganese and iron in the sample obtained after the test maintained a homogeneous distribution without element segregation. The results indicate that iron-substituted Mn_2O_3 prepared using the Pechini process has a reproducible thermochemical storage performance and durability without degradation during high-temperature thermal cycling.

Figure S1a shows an equilibrium diagram of the Mn-Fe-O system ($P_{\text{O}_2} = 0.168 \text{ atm}$). The 20 mol% iron-substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ redox pair underwent a phase transition between a bixbyite structure and a spinel structure by the swing temperature method of $T = 700\text{--}1050^\circ\text{C}$ in a gas mixture with a constant P_{O_2} . The swing temperatures of $T = 700\text{--}1050^\circ\text{C}$ were selected as sufficiently lower and higher than the phase-transition temperature in this study. The non-isothermal HD mode, which involves decreasing the temperature with a constant oxygen partial pressure, kinetically decreases the HD rate with the progress of the HD mode; however, it is thermodynamically favorable because of the exothermic process. Thus, to ensure the reaction time of the HD mode, a low temperature of $T = 700^\circ\text{C}$, as compared with the phase transition at the equilibrium state, was selected in this study. In contrast, a high temperature of $T = 1050^\circ\text{C}$ was selected to ensure the complete phase transition of the bixbyite structure into a spinel structure during the HC mode. Figure S1b,c shows the XRD patterns of the as-prepared and thermal-cycled samples, respectively. The series of peaks for both samples corresponded to the bixbyite-type structure. All diffraction peaks corresponding to the bixbyite-type structure were indexed to cubic unit cells (space group $\text{I } 21\ 3\ (199)$), and the lattice cell parameters of the samples were determined by the Rietveld refinement of the structure model. The lattice parameters ($a = 9.418(5) \text{ \AA}$ for the as-prepared sample and $a = 9.421(1) \text{ \AA}$ for the long-term thermal-cycled sample) were higher than those ($a = 9.410(0) \text{ \AA}$) obtained for the non-substituted $\alpha\text{-Mn}_2\text{O}_3$ (COD ID no. 96-901-4249). This result indicates that both samples formed and retained a solid solution of $(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3$ during long-term thermal cycling.

Reversible thermochemical storage using the redox pair $(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3/(\text{Mn}_{0.8}\text{Fe}_{0.2})_3\text{O}_4$ can be expressed as:



where O_2 in the gas stream plays an important role as the gaseous oxidant in heat-transfer fluid (air) for the TES system of the CSP plant.

3.2. HD Kinetics of the Long-Term Thermal-Cycled Sample

Figure 2 shows TG-DTA curves of (a) the as-prepared and (b) the long-term thermal-cycled samples obtained using the temperature swing method under a constant gas flow rate and oxygen partial pressure. The kinetics of both samples were examined, evaluated, and compared using the same temperature program in the TG-DTA reactor. In the temperature swing test for kinetic analysis, a temperature swing between 1050 and 650 °C was conducted for both samples to approach the complete termination of the HD mode as much as possible. When the weights of both samples increased during the HD mode, an exothermic peak in the DTA curves appeared at the cooling rates of 3–7 K/min for both samples. For the as-prepared sample (Figure 2a), the weight change for all runs (3.6–3.7%) exceeded the theoretical change of the non-substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ (3.378%). The theoretical value was calculated using the thermodynamic equilibrium software program FactSage [77]. The reason for the variation in the weight change may be the unstable morphology of the sample at high temperatures and the iron substitution into Mn_2O_3 . The weight change for the as-prepared sample returned to 99.8–99.6% of the initial weight during the HD mode. The results of the as-prepared sample indicate that thermally reduced $(\text{Mn}_{0.8}\text{Fe}_{0.2})_3\text{O}_4$ was oxidized by O_2 in the gas stream and was almost completely converted into $(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3$ with a phase transition. For the long-term thermal-cycled sample (Figure 2b), the weight change (99.2–99.0% of the initial weight) during the HD mode deteriorated, as compared with that of the as-prepared sample. These results indicate that the morphology of the sample affects the kinetics of the HD mode due to secondary aggregation at high temperatures.

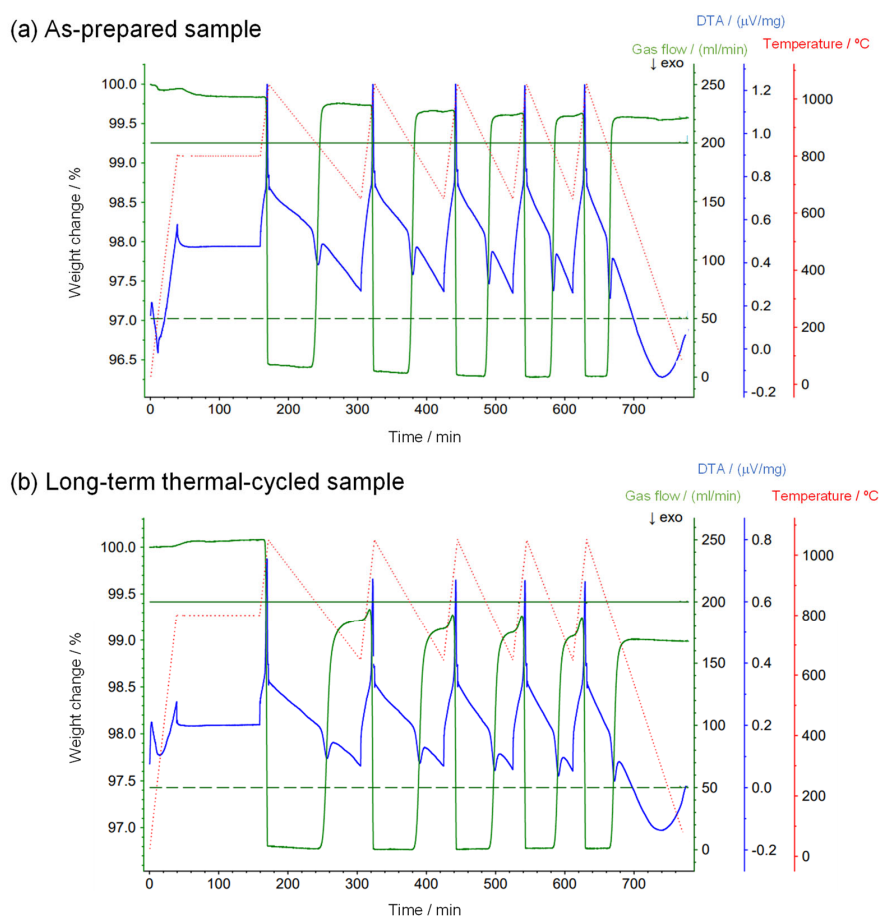


Figure 2. TG–DTA curves of (a) the as-prepared and (b) long-term thermal-cycled samples using the temperature swing method with an oxygen partial pressure of $P_{\text{O}_2} = 0.168$ bar. The red dotted line is a temperature profile.

Figure 3 shows the plots of the apparent activation energy (E_a) of both samples in the HD mode. The values were estimated with $\Delta\alpha = 0.01$ to confirm the variation of the reaction model during the HD mode. Additionally, to confirm the repeatability and fluctuation of the estimated value, the as-prepared sample was tested twice, and the values of E_a were estimated and compared. For the as-prepared sample, the results of the first and second tests showed that the value of E_a tended to gradually decrease with the progress of the HD mode. The average value (AVE) and standard deviation (SD) of E_a for the first and second tests were AVE = 228.97 kJ/mol (SD = 65.7 kJ/mol) and AVE = 231.49 kJ/mol (SD = 64.4 kJ/mol) in the range of $\alpha = 0$ –0.92, respectively. The final stage of the HD mode, corresponding to $\alpha = 0.92$ –1.0, was excluded from the estimation of E_a because a large fluctuation in the value of E_a was observed for both samples. The reproducible tendency of the E_a values indicates that the rate-determining step of the HD mode varied with the progress of the HD mode.

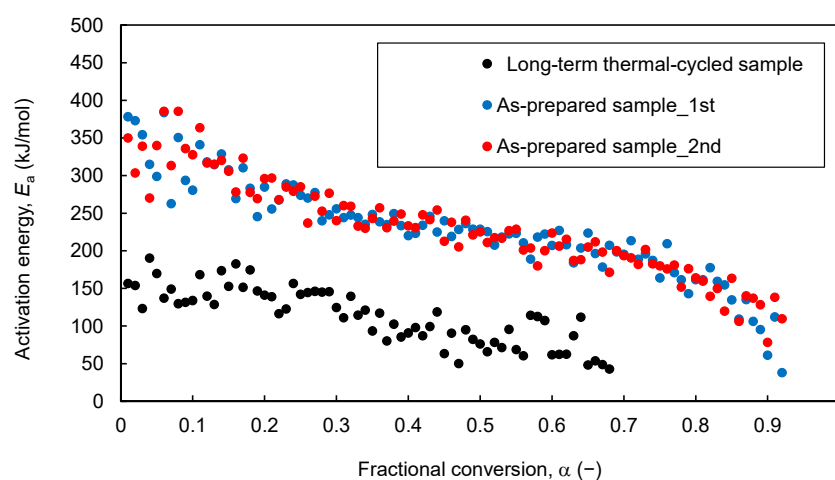


Figure 3. Plots of the apparent activation energy (E_a) of both samples during the progress of the HD mode. The values were plotted with $\Delta\alpha = 0.01$ to monitor the variation of the kinetic model.

The AVE and SD values of E_a for the long-term thermal-cycled sample were 112.96 and 37.3 kJ/mol in the range of $\alpha = 0$ –0.68, respectively. As described above, the sample weight change during the HD mode was 99.2–99.0% of the initial weight (Figure 2b), which corresponds to 70.3–76.3% of the theoretical value (a weight change of 3.37% was estimated using Equations (13) and (14)). Therefore, the estimated E_a for the sample was limited to $\alpha < 0.70$. The AVE and SD values of E_a for the samples were lower than those for the as-prepared samples. As shown in Figure 1e–h, the sample subjected to a long period of high-temperature testing had already formed a thermally stable morphology and element distribution. This result indicates that the sintered structure composed of secondary aggregates stabilizes the E_a value with a small SD value through the total range of α with temperature during the HD mode. Additionally, the small AVE values of E_a for the sample indicate that the kinetics of the HD mode progressed by different mechanisms from those of the as-prepared sample. Thus, the authors were challenged for identifying the transition of the kinetic model function of $f(\alpha)$ during the HD mode.

Figure 4 shows the master plot analysis of the HD mode for the long-term thermal-cycled sample when cooled at (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min from 1050 to 650 °C. Before the kinetic testing of the HD mode, preliminary testing was performed to investigate various cooling rates of 3–20 K/min in the HD mode. Consequently, slow cooling rates were applied to acquire as much kinetic data as possible in the HD mode. Theoretical curves of $\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}}$ against α were compared with experimental data plots of $\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}}$. Comparative observation of fitting is an effective screening process for simultaneously evaluating multiple candidates and selecting a possible model from among them. Candidates for the theoretical model function ($f(\alpha)$) are cited in [78,79]. The theoretical models to

match the data plots for all cooling rates shift during the progress of fractional conversion (Figure 4). For example, in an observation of visual pattern fitting, the experimental data of the cooling rate of 3 K/min (Figure 4a) fits the A2 and A3 models (light yellow and gray curves) in the initial stage of $\alpha = 0\text{--}0.20$, lies between the R2, R3, and F1 models (dark green, dark blue, and light green curves) in the middle stage of $\alpha = 0.25\text{--}0.50$, and positions on the D3, D4, F2, and F3 models (dark yellow, light blue, light indigo, and orange curves) in the middle/final stage of $\alpha = 0.50\text{--}0.65$. A similar tendency appears in the pattern fitting in the experimental data at 4–7 K/min (Figure 4b–e).

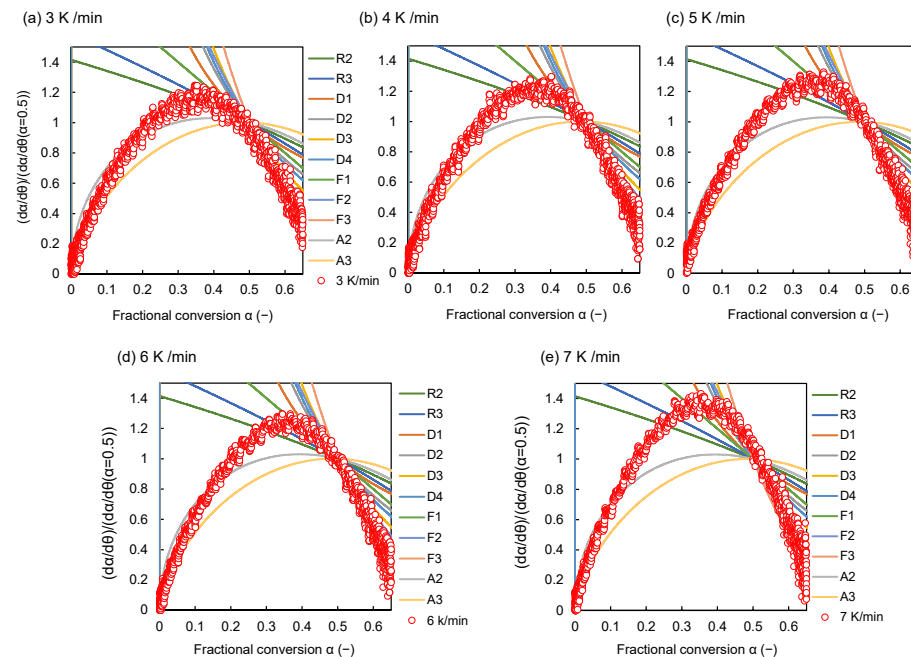


Figure 4. Non-isothermal master plots of the thermal-cycled sample at cooling rates of (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min. The red open circles (experimental data) and colored curves (possible theoretical model) were compared.

The selected candidate models were compared in each initial/middle/final stage with the experimental data for all the cooling rates. Figure 5 shows the partially enlarged master plot in the ranges of (a) $\alpha = 0\text{--}0.25$, (b) $\alpha = 0.25\text{--}0.50$, and (c) $\alpha = 0.50\text{--}0.65$. The experimental data for all cooling rates are plotted for comparison in the figure. In the early stage (Figure 5a), a series of data initially lies on the A3 model, then distributes between models A3 and A2, and positions beyond the A2 model at the end. In the middle stage (Figure 5b), the data group shifted in the order of the R2, R3, and F1 models with an increasing fractional conversion of α . In the middle/final stage (Figure 5c), the data group lies on all of the models at $\alpha = 0.50$. Subsequently, the F3 model was dominant at $\alpha = 0.65$. However, it is difficult to determine suitable models among the strong candidates for visual data fitting. Thus, the authors used a residual sum of squares (RSS) method to identify a well-described theoretical model. The detailed description of the RSS methods is referred in the paper [72]. Figure S2 shows the variations in the RSS values relative to the cooling rate. The A2 model had minimal RSS value for all cooling rates in the range of $\alpha = 0\text{--}0.25$ (Figure S2a). In the ranges of $\alpha = 0.25\text{--}0.50$ and $0.50\text{--}0.65$, the RSS values for the R2 and F3 models were preferable among the candidate models in the cooling rates of $\beta = 3\text{--}6$ K/min, respectively (Figure S2b,c). Therefore, the authors decided that the best theoretical models in the HD mode are the A2 model ($\alpha = 0\text{--}0.25$), the R2 model ($\alpha = 0.25\text{--}0.50$), and the F3 model ($\alpha = 0.50\text{--}0.65$).

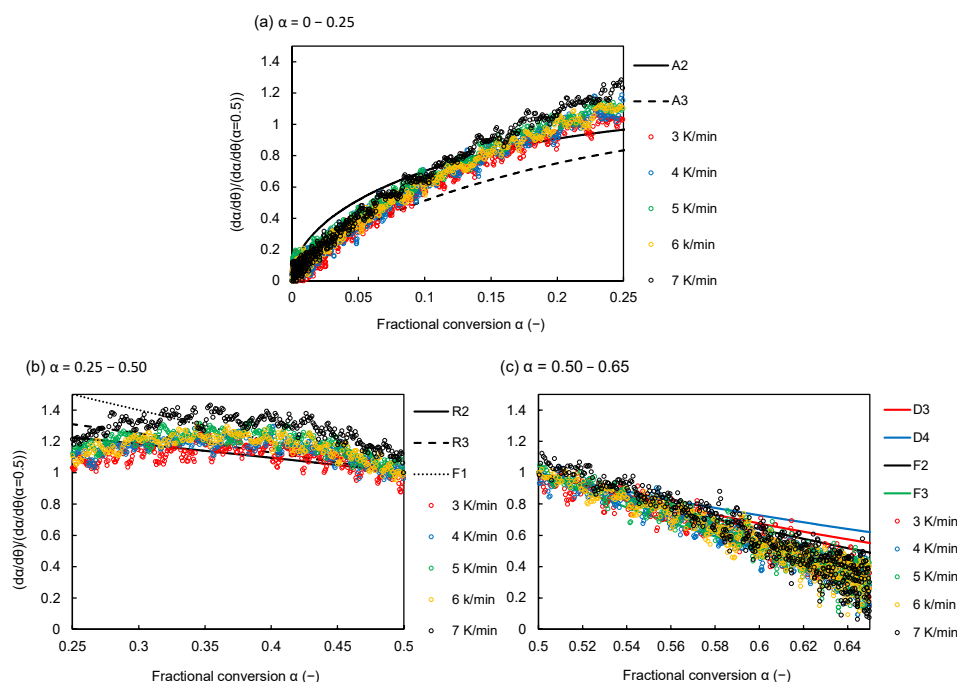


Figure 5. Comparison between the candidate theoretical models (lines) and experimental data (open circles) in the master plot. All experimental data were plotted against the fractional conversion of α in the (a) initial stage of $\alpha = 0\text{--}0.20$, (b) middle stage of $\alpha = 0.25\text{--}0.50$, and (c) middle/final stage of $\alpha = 0.50\text{--}0.65$.

The pre-exponential factor (A) can be calculated using the estimated apparent activation energy (E_a) and corresponding model function ($f(\alpha)$) for each range of α . According to the Arrhenius kinetic law, the value of A should generally become constant within a limited temperature range when the estimated model and activation energy do not vary in the temperature range. To evaluate whether the value of A for each model depended on the temperature in the limited range of α , the value of A for all estimated models was plotted against the temperature. The results of the temperature dependence are shown for all cooling rates in Figures S3–S7. It appears that the plot of the A values for all the estimated models lay on an almost constant value without temperature dependence. To quantitatively compare the scattering in the plot of the A value among all the estimated models, the coefficient of variation (CV) was used as an index for the scattering of the calculated data (Figure S8). The results show that the plots of the A value for all cooling rates had a similar degree of variation, owing to the small value of CV (<0.1) for all of the estimated models. Thus, the A value plot was considered to be constant for all estimated models within the limited temperature range.

Figure 6 shows the relationship between the estimated A values of the (a) A2, (b) R2, and (c) F3 models and the cooling rates of $\beta = 3\text{--}7$ K/min during the HD mode. To evaluate the scattering of the AVE of A , the SD values of A in an average were shown as error bars in the plot. The values of A for all the models monotonically increased with the cooling rate, and the squares of the correlation coefficient (R^2) for the linear regression were 0.9995 (A2 model), 0.9998 (R2 model), and 0.9946 (F3 model). The results of the small SD values and linearity ($R^2 \approx 1$) for all models indicate that A for all models depends on the cooling rate of β , leading to the incorporation of the rate equation. This is the first report of an HD kinetic analysis of non-substituted and substituted manganese oxides. According to the transition state and collision theories based on the kinetic theory of gas–gas, the pre-exponential factor (A) depends on temperature with a certain power of n ; however, it is independent of the cooling rate of β . Thus, it is likely to be influenced by the test methods. In the case of the HC mode [72], the estimated pre-exponential factor (A) of all models was almost

constant with variations in the heating rates. The difference in the cooling/heating rates between the HD and HC modes may be ascribed to both reaction mechanisms. The HC mode released oxygen gas from the oxide under an atmospheric gas stream with a constant P_{O_2} during the heating process in the TGA reactor. In contrast, in the present HD mode, the thermally reduced solid sample placed in the crucible directly reacted with the gaseous oxygen contained in the gas stream during the cooling process. The configuration of the TGA equipment may affect the accessibility between the solid reactant and gaseous species, leading to a pre-exponential factor (A). A detailed comparison of the HD kinetics with those reported in the literature is discussed in the following section. Therefore, the kinetics equation of the HD mode in the gas stream is

$$\text{A2 model: } \frac{d\alpha}{dt} = (4.33\beta + 3.79) \times 10^6 \exp\left(-\frac{1.48 \times 10^5}{RT}\right) \times 2(1-\alpha)[- \ln(1-\alpha)]^{\frac{1}{2}} \quad (15)$$

$$\text{R2 model: } \frac{d\alpha}{dt} = (1.65\beta + 3.38) \times 10^3 \exp\left(-\frac{1.06 \times 10^5}{RT}\right) \times 2(1-\alpha)^{1/2} \quad (16)$$

$$\text{F3 model: } \frac{d\alpha}{dt} = (1.09\beta + 4.78) \times 10^3 \exp\left(-\frac{8.05 \times 10^4}{RT}\right) \times (1-\alpha)^3 \quad (17)$$

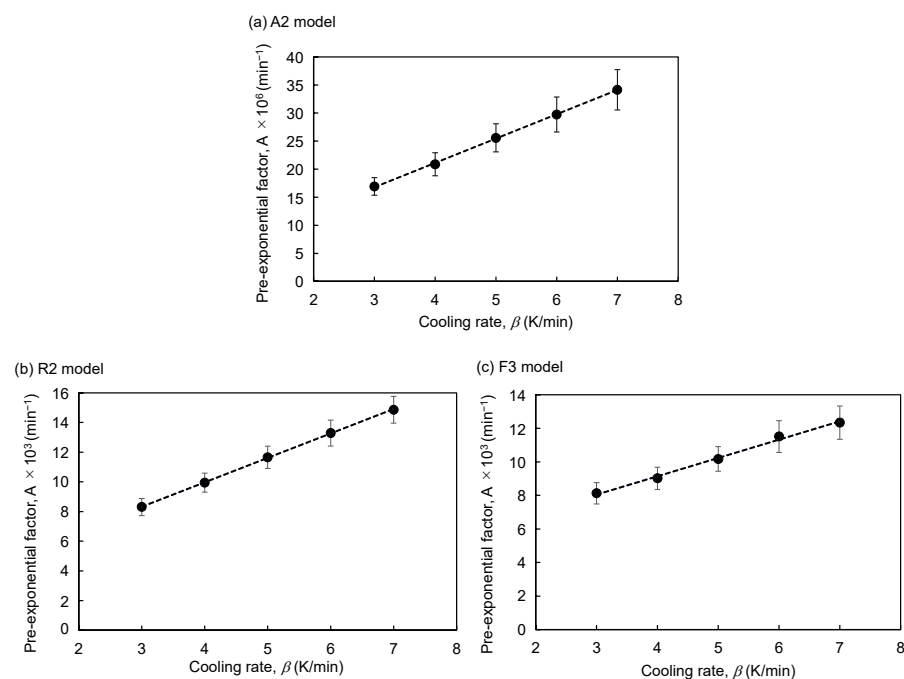


Figure 6. Relationship between the pre-exponential factor (A) and cooling rate (β) for the long-term thermal-cycled sample. The results of the (a) A2, (b) R2, and (c) F3 models are shown in this figure. The error bar in all plots displayed in the solid circle is the SDs in the designated fractional conversion ranges.

The E_a value for each predicted kinetic model was estimated as the AVE within the applicable range of α . Namely, the average E_a values were $148.37 \text{ kJ}\cdot\text{mol}^{-1}$ in the range of $\alpha = 0-0.25$, $106.25 \text{ kJ}\cdot\text{mol}^{-1}$ in the range of $\alpha = 0.25-0.50$, and $80.46 \text{ kJ}\cdot\text{mol}^{-1}$ in the range of $\alpha = 0.50-0.65$, and were given to the formulation of the A2, R2, and F3 models, respectively. The SD values for the average E_a were 19.22 , 26.53 , and $21.67 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. These SD values are smaller than that ($37.3 \text{ kJ}\cdot\text{mol}^{-1}$) in the range of $\alpha = 0-0.65$. Additionally, the SV values of 0.130 , 0.250 , and 0.270 were smaller than that (0.330) in the range of $\alpha = 0-0.65$. These results indicate that the average E_a with small scattering can be applied to Equations (15)–(17).

Figure 7 shows the validation of the predicted A2, R2, and F3 models with the experimental fractional conversion at each cooling rate. Figure 7a shows that for a cooling rate of 3 K/min, the predicted three models match well in each range. Due to the fact that $\alpha = 0.65$, the predicted F3 model is not compatible with the experimental data because the long-term thermal-cycled sample in the region of $\alpha = 0.65$ –1.0 is an imperfect oxidation owing to the very slow discharging kinetics. As seen in Figure 7b–e, for cooling rates of 4–7 K/min, the predicted models, in order of the A2, R2, and F3 models, describe the experimental data well. These results indicate that the predictive models for the cooling rates agreed well with the experimental data. This shows the validity of the estimated model to describe the HD kinetics of $(\text{Mn}_{0.8}\text{Fe}_{0.2})_3\text{O}_4$ in Equation (14).

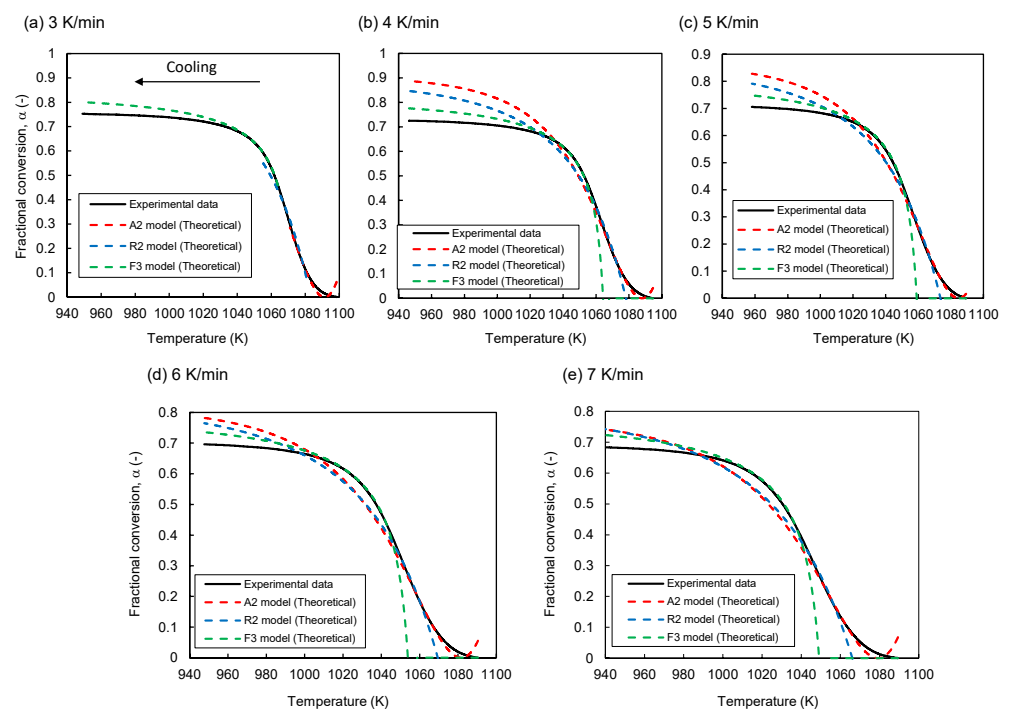


Figure 7. Validation of the predicted models (red, blue, and green broken curves for the A2, R2, and F3 models, respectively) with the experimental fractional conversion (black curve) for the long-term thermal-cycled sample at the cooling rates of $\beta =$ (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min. The curves are compared to validate the predicted models.

3.3. HD Kinetics of the As-Prepared Sample

The HD kinetics of the as-prepared sample were analyzed using the same methodology as that used in Section 3.2. Figure 8 shows the master plot of the HD kinetics of the as-prepared sample when cooled at different rates of 3–7 K/min. In the first half of the HD mode of $\alpha = 0$ –0.50, the theoretical P2, P3, or B1 models fit all of the experimental data, in contrast to the different cooling rates. These results indicate that the morphology of the sample affected the kinetic mechanism in the first half of the HD mode. The potential reasons are: (1) a time-dependent variation of sample morphology during the first half of the HD mode due to the aggregation and sintering of initial particles, and (2) the formation of a particle–particle connection structure in the sample during the HD mode, leading to the development of multiple oxygen-uptake pathways. Further investigations are required in the future to elucidate the relationship between the morphology of the sample and its kinetic mechanism. In the HD mode of $\alpha = 0.50$ –1.0, as shown in Figure 8, it appears that the experimental data does not correspond to all the theoretical models; however, the closest theoretical model to the data is the A4 model. The results indicate that the kinetic mechanism of the as-prepared sample changed over time (temperature decrease) in the HD mode.

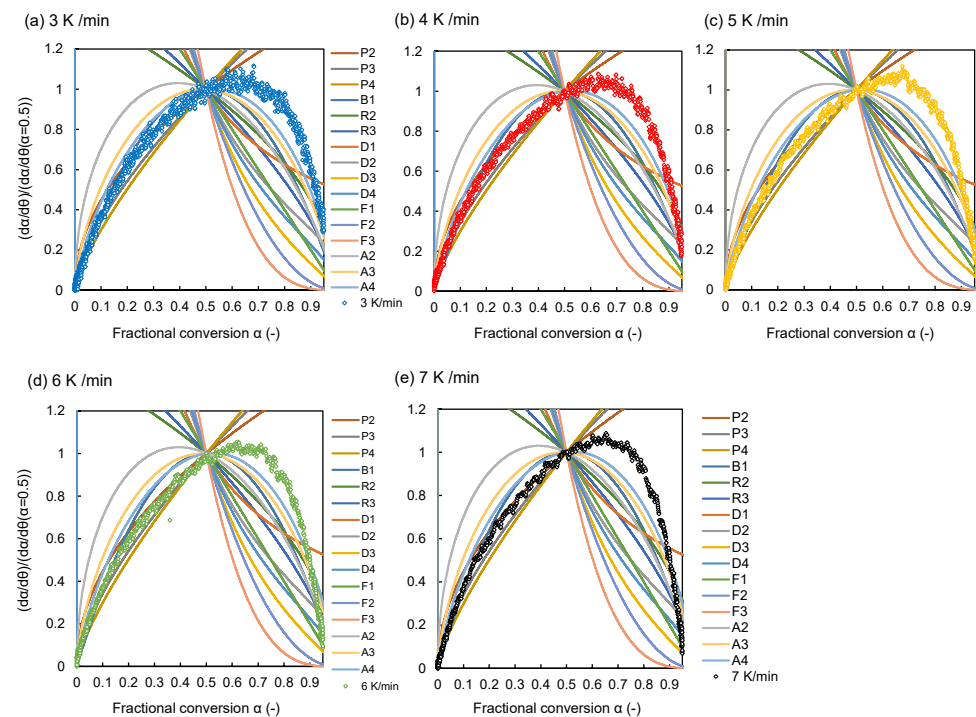


Figure 8. Non-isothermal master plots of the as-prepared sample during the HD mode at the cooling rates of (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min. The colored open rhombs (experimental data) and colored curves (theoretical model) were compared to estimate which model best fitted the experimental data.

To quantitatively evaluate the suitability of the estimated models against the experimental data at different cooling rates and select an appropriate model to describe the data, the RSS values for models P2, P3, and B1 were calculated and compared (Figure 9). The RSS value for the P2 model was the smallest for the cooling rates of 3–5 and 7 K/min, whereas those for the P2 and P3 models for the cooling rate of 6 K/min were only marginally different (14%). The results show that the P2 model can advantageously explain the kinetics of the first half of the HD mode at all cooling rates.

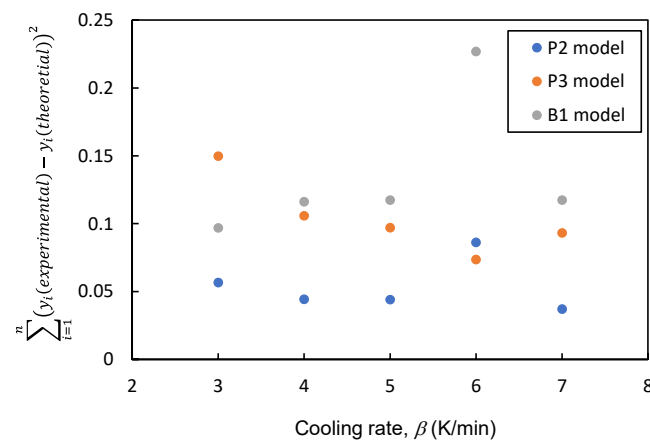


Figure 9. Comparison of the RSS values of the estimated P2, P3, and B1 models against variations of the fractional conversion for the first half of the HD mode. The RSS values between the experimental kinetic data of the as-prepared sample and the predicted theoretical models were calculated against various cooling rates of β .

The values of A for the predicted P2 and A4 models for the as-prepared sample were calculated. Figures S9 and S10 show plots of the calculated A values of the P2 and A4 models against the temperature variations for each cooling rate. The value of A was estimated for the P2 model in the temperature range of the first half of the HD mode ($\alpha = 0.1$ – 0.50) and for the A4 model in the temperature range of the latter half of the HD mode ($\alpha = 0.5$ – 1.0). As shown in Figure S9, the value of A tended to increase slightly as the HD mode progressed (temperature decreases); however, the plot of A for the P2 model was almost constant without temperature dependence. As shown in Figure S10, and for the P2 model, the plot of A for the A4 model was almost independent of the temperatures corresponding to the latter half of the HD mode for all cooling rates. These results indicate that the value of A in all tentative models can be estimated as a constant value under the designated temperature range and cooling rate.

Figure 10 shows the relationship between the AVE of the estimated pre-exponential factor (A) for the as-prepared sample and the cooling rates of $\beta = 3$ – 7 K/min during the HD mode. The results for the (a) P2 and (b) A4 models are shown together with the averaged SD values (vertical error bars) of A in the plot. The values of A for all models monotonically increased with the cooling rate, and the R^2 values for the linear regression were 0.9960 (P2 model) and 0.9985 (A4 model). The A values for models P2 and A4 were formulated as a function of the cooling rate, and the HD kinetics of the as-prepared samples were as follows:

$$\text{P2 model : } \frac{d\alpha}{dt} = \left(1.75\beta - 1.88 \right) \times 10^{10} \exp \left(-\frac{2.47 \times 10^5}{RT} \right) \times 2\alpha^{1/2} \quad (18)$$

$$\text{A4 model : } \frac{d\alpha}{dt} = \left(6.92\beta - 4.31 \right) \times 10^7 \exp \left(-\frac{1.97 \times 10^5}{RT} \right) \times 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4} \quad (19)$$

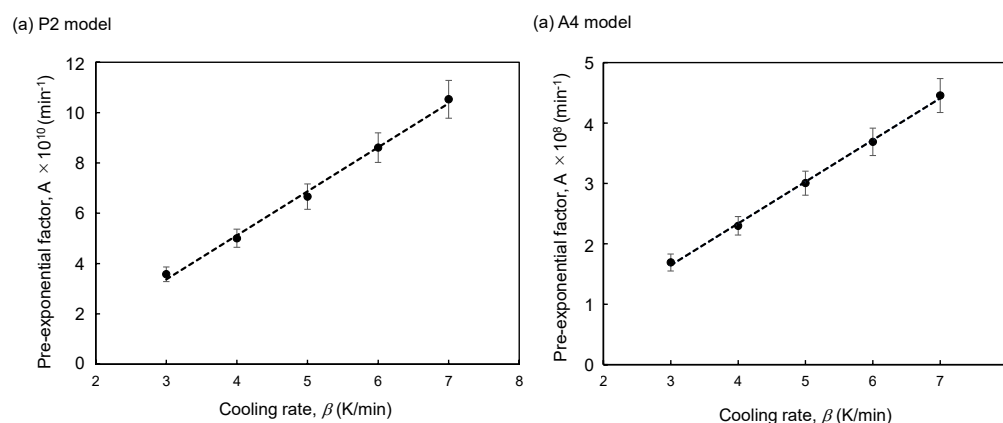


Figure 10. Estimated A values of the (a) P2 and (b) A4 models against cooling rate of β . Error bar in both plots is the SDs in (a) the first half of the HD mode ($\alpha = 0.1$ – 0.50) and (b) the latter half of the HD mode ($\alpha = 0.50$ – 1.0).

Figure 11 shows the validation of the predicted P2 and A4 models of the HD kinetics and compares them with the experimental fractional conversions. The predicted P2 model, as compared with the predicted A4 model, for all cooling rates fitted well in the range of $\alpha = 0$ – 0.50 . The predicted A4 model accurately expressed the data curve in the latter half of the HD mode. These results indicate that the predicted HD mode models agreed well with the experimental data. The small deviation in the final stage of $\alpha = 0.95$ – 1.0 may be due to the deviation from the A4 model, the lower activation energy than the AVE, or the slow internal diffusion of the oxygen absorbed by the sample in the equipment.

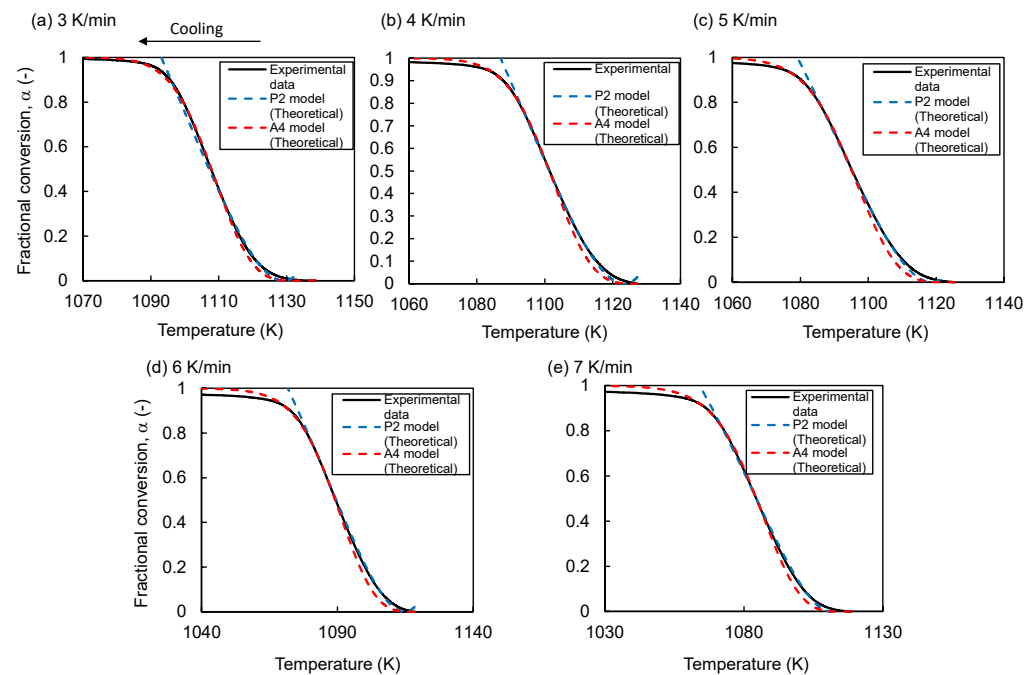


Figure 11. Validation of the predicted theoretical models (blue and red broken curves for the P2 and A4 models, respectively) with the experimental fractional conversion (black curve) for the as-prepared sample at cooling rates of $\beta =$ (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min. The curves are compared to validate the predicted model.

3.4. Comparison with Previous Studies on HD Kinetics

In this section, the HD kinetic results for both samples are compared with those of previous kinetic data in the literature. Table 1 summarizes the iron substitution level, test atmosphere, estimated reaction model, Arrhenius parameters, and kinetic equation in the HD mode. The kinetic data were obtained from previous studies [66,67,73,74]. For non-substituted Mn_3O_4 [73], the R3 model was estimated by an isothermal oxidation process at a constant and high O_2 level (pure O_2 , $P_{\text{O}_2} = 100$ kPa) at a low temperature of $T = 162$ – 290 °C, and the value of E_a differed from the temperature level. The reason for this is the different oxidation mechanisms depending on the temperature level: the formation of the defect spinel phase of the Mn_2O_3 type ($T < 210$ °C) and a structural transformation leading to the Mn_5O_8 type (240 °C $< T$). From the viewpoint of chemical composition in this study, the HD kinetics were observed for the 20% and 25% iron substitution samples [66,67]. The HD kinetics of the 25% substitution sample was examined using isothermal oxidation at various P_{O_2} pressures and temperatures. The kinetic equation was formulated under a high-temperature level of 800 °C $< T$ and a limited pressure level of 15 kPa $< P_{\text{O}_2} < 40$ kPa [67]. The 20% substitution sample was also investigated using an isothermal oxidation process at 650 – 800 °C under air flow. The HD kinetics followed the Arrhenius behavior in the temperature range 650 – 725 °C, whereas a non-Arrhenius behavior was observed in the temperature range 725 – 800 °C [66]. The HD kinetics for the 20% and 25% iron substitution samples were estimated using the Avrami–Erofeev mechanism with different Arrhenius parameters. These results indicate that the HD mechanism can change with the temperature range and iron substitution level. In the case of the 67% iron substitution sample, the HD kinetics were studied using non-isothermal oxidation at heating rates of 2.5 – 10 °C/min in the temperature range 50 – 1000 °C under an air atmosphere [74]. The HD kinetic models of the sample were different from the fractional conversion range, namely the D3 model ($\alpha = 0$ – 0.30) and A0.5 ($\alpha = 0.3$ – 0.8). The results indicated that the kinetic model and Arrhenius parameters varied as the HD mode progressed. In this study, it was observed that the HD kinetic models and Arrhenius parameters for both samples changed as the fractional conversion progressed. Additionally, the effect of the HD kinetics on long-term thermal

cycling was evaluated in this study. The results of the present study show that the morphology of the sample strongly affects the HD mechanism including Arrhenius parameters, and the rate-determining step of the HD mode shifts together with the progression of fractional conversion; that is, independently of sample morphology. These characteristics are in good agreement with the results presented in Table 1. This is of particular concern when HD kinetics are studied under a limited gas-solid contact in the test equipment. In addition to the test conditions described above, the relationship between the gas flow direction and the sample mounted in the crucible of the equipment changes the accessibility of the gas-solid, as discussed in the literature. Thus, it is necessary to pay full attention to the important factors governing HD kinetics in comparison with the previous results.

In the thermal-cycled sample, the A2 model explained the HD kinetics for $\alpha = 0$ –0.25, whereas the R2 model fitted best for $\alpha = 0.25$ –0.50. According to the HC kinetics analyses in our previous study, which were evaluated using the same sample under the same test conditions/equipment [72], the best estimated models for the HC mode were the A2 model in the initial/middle stage ($\alpha = 0.20$ –0.48) and the R2 model in the middle/final stage ($\alpha = 0.49$ –1.0). This suggests that the long-term thermal-cycled sample exhibits a kinetic mechanism regardless of the HD and HC modes in the reversible thermochemical TES, which can vary from A2 to R2 with the fractional conversion. This may be due to the microstructural characteristics of the samples, with long-term thermal and morphological stability at high temperatures. In contrast, in the as-prepared sample, the best-estimated models were the contracting volume (R3) model that fitted to the HC mode at $\alpha = 0.2$ –1.0, and a first-order (F1) model that fitted to $\alpha = 0.4$ –1.0. There are no common kinetic models for the HC and HD modes of reversible thermochemical TES processes.

In the thermal-cycled sample, the A2 model that fitted in the initial stage of $\alpha = 0$ –0.25 can be formally understood as an instantaneous random nucleation and two-dimensional spread oxidative reaction of $(Mn_{0.8}Fe_{0.2})_3O_4$ from the surface of the three-dimensionally sintered morphology [80]. That the R2 model fitted in the initial/middle stage of $\alpha = 0.25$ –0.50 means that the nucleation and oxidative reactions occur continuously and spread within the contracting region of the cylindrical network structure of three-dimensionally connected particles. Finally, that the F3 model fitted in the middle/final stage of $\alpha = 0.50$ –0.65 means that the oxidative reaction proceeds homogeneously inside the agglomeration of particles proportional to the value of α , raised to a power that represents the reaction order [78].

Table 1. Kinetic equations of the HD mode for the kinetic data of this study and previous studies using non- and iron-substituted samples. The kinetic data for the non-substituted samples are listed as a comparison.

Material	Atmosphere	Reaction Model	Activation Energy (kJ/mol)	Pre-Exponential Factor [1/min]	Equation(d α /dt)	Reference
As-prepared sample (Mn _{0.8} Fe _{0.2}) ₃ O ₄	Non-isothermal oxidation with different cooling rates of 3–7 °C/min from 1050 °C to 650 °C in a constant O ₂ atmosphere (P _{O₂} = 16.8 kPa).	P2 (α = 0.10–0.50)	247.00 (SD = 24.14)	$(1.75 - 1.88) \times 10^{10}$	$\frac{d\alpha}{dt} = (1.75\beta - 1.88) \times 10^{10} \exp\left(-\frac{2.47 \times 10^5}{RT}\right) \times 2\alpha^{1/2}$	Present study
		A4 (α = 0.50–1.0)	196.61 (SD = 19.18)	$(6.92 - 4.31) \times 10^7$	$\frac{d\alpha}{dt} = (6.92\beta - 4.31) \times 10^7 \exp\left(-\frac{1.97 \times 10^5}{RT}\right) \times 4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	
Long-term cycled sample (Mn _{0.8} Fe _{0.2}) ₃ O ₄		A2 (α = 0–0.0.25)	148.37 (SD = 19.22)	$(4.33 + 3.79) \times 10^6$	$\frac{d\alpha}{dt} = (4.33\beta + 3.79) \times 10^6 \exp\left(-\frac{1.48 \times 10^5}{RT}\right) \times 2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	
		R2 (α = 0.25–0.50)	106.25 (SD = 26.53)	$(1.65 + 3.38) \times 10^3$	$\frac{d\alpha}{dt} = (1.65\beta + 3.38) \times 10^3 \exp\left(-\frac{1.06 \times 10^5}{RT}\right) \times 2(1 - \alpha)^{1/2}$	
		F3 (α = 0.50–0.65)	80.46 (SD = 21.67)	$(1.09 + 4.78) \times 10^3$	$\frac{d\alpha}{dt} = (1.09\beta + 4.78) \times 10^3 \exp\left(-\frac{8.05 \times 10^4}{RT}\right) \times (1 - \alpha)^3$	
(Mn _{0.33} Fe _{0.67}) ₃ O ₄	Non-isothermal oxidation with different heating rates of 2.5–10 °C/min from 50 °C to 1000 °C under air stomosphere. (HC mode was performed at 1200 °C unfer N ₂ atmosphere.)	D3 (a = 0–0.30)	192 ± 2	log(A) = 11.75 ± 0.04	-	[74]
		A0.5 (a = 0.30–0.8)	181.4 ± 0.3	log(A) = 9.65 ± 0.06	-	
(Mn _{0.8} Fe _{0.2}) ₃ O ₄	Isothermal oxidation at 650–800 °C under air flow. (HC mode was performed up to 1000 °C unfer Ar atmosphere.)	A3	74 ± 7	2.3×10^3	$\frac{d\alpha}{dt} = 2.3 \times 10^3 \exp\left(-\frac{74}{RT}\right) \alpha^{1.26} \times (1 - \alpha)^{0.522} [- \ln(1 - \alpha)]^{-0.59}$ (T < 725 °C)	[66]
Mn ₃ O ₄	Isothermal oxidation in a P _{O₂} = 100 kPa at T = 162–290 °C	R3	60 (T < 210 °C) 95 (240 °C < T)	-	Isothermal oxidation: the formation of the defect spinel phase of Mn ₂ O ₃ type (T < 210 °C) a structural transformation leading to Mn ₅ O ₈ (240 °C < T)	[73]
(Mn _{0.75} Fe _{0.25}) ₃ O ₄	Isothermal oxidation in a different O ₂ atmosphere (P _{O₂} = 5.1, 10.1, 20.4, 40.4 and 71.1 kPa)	AE (n = 1.38)	463.35	1.07×10^{18}	$\frac{d\alpha}{dt} = 1.07 \times 10^{18} \exp\left(-\frac{463.53}{RT}\right) \times 1.38(1 - \alpha)[- \ln(1 - \alpha)]^{(1 - \frac{1}{1.38})} \times \left(\ln \frac{P_{O_2}}{P_{O_2}(T)}\right)^{7.06}$	[67]

4. Summary

The morphology, elemental distribution, and HD kinetics of the 20 mol% iron-substituted $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ redox pair over 360 runs of thermochemical energy storage were investigated and analyzed under a non-isothermal process using a temperature swing process at atmospheric pressure with a constant oxygen partial pressure. The kinetic analysis of the HD mode for the sample subjected to the long-term thermal cycling test was compared with that of the as-prepared sample evaluated using the same test device under the same kinetic methodology. Finally, the HD kinetic data in this study were compared with HD kinetics examined under various test conditions in previous studies.

A round-shaped aggregation appeared in the long-term thermal-cycled sample, as compared with the as-prepared sample, which is grain growth and coarsening, similar to the three-dimensionally connection of the porous body. The sample obtained after the long-term thermal-cycling test maintained a homogeneous distribution without element segregation. The sample exhibited a reproducible thermochemical storage performance and durability without degradation during thermal cycling at high temperatures. Thus, the reversible thermochemical storage using the redox pair proceeded repeatedly.

The HD kinetics of the long-term thermal-cycled and as-prepared samples were examined, evaluated, and compared using the same temperature program in the TG-DTA reactor. Significantly, the HD kinetic mechanism for both samples was different and varied with a progressing fractional conversion. The discharging modes of the long-term thermal-cycled sample were the A2 model ($\alpha = 0\text{--}0.25$), contracting area (R2) reaction model ($\alpha = 0.25\text{--}0.50$), and third-order (F3) reaction model ($\alpha = 0.50\text{--}0.65$). The discharging modes for the as-prepared sample were the power law (P2) reaction model ($\alpha = 0.1\text{--}0.50$) and the Avrami–Erofeev (A4) reaction model ($\alpha = 0.5\text{--}1.0$). The predicted kinetic equations for both samples agreed well with the experimental kinetic data.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/en16083367/s1>, Figure S1: (a) Equilibrium diagram of the Mn-Fe-O system ($P_{\text{O}_2} = 0.168$ atm) and the XRD patterns of (b) the as-prepared and (c) the long-term thermal-cycled samples in the 2θ range; Figure S2: Variations of the RSS values against the cooling rates of $\beta = 3\text{--}6$ K/min. (a) $\alpha = 0\text{--}0.25$, (b) $\alpha = 0.25\text{--}0.50$, and (c) $\alpha = 0.50\text{--}0.65$; Figure S3: Variations of pre-exponential factor A against temperatures for the (a) A2 model, (b) R2 model, and (c) F3 model, respectively. The long-term thermal-cycled sample was subjected to the heat-discharging process at a cooling rate of $\beta = 3$ K/min.; Figure S4: Variations of pre-exponential factor A against temperatures for the (a) A2 model, (b) R2 model, and (c) F3 model, respectively. The long-term thermal-cycled sample was subjected to the heat-discharging process at a cooling rate of $\beta = 4$ K/min.; Figure S5: Variations of pre-exponential factor A against temperatures for the (a) A2 model, (b) R2 model, and (c) F3 model, respectively. The long-term thermal-cycled sample was subjected to the heat-discharging process at a cooling rate of $\beta = 5$ K/min.; Figure S6: Variations of pre-exponential factor A against temperatures for the (a) A2 model, (b) R2 model, and (c) F3 model, respectively. The long-term thermal-cycled sample was subjected to the heat-discharging process at a cooling rate of $\beta = 6$ K/min.; Figure S7: Variations of pre-exponential factor A against temperatures for the (a) A2 model, (b) R2 model, and (c) F3 model, respectively. The long-term thermal-cycled sample was subjected to the heat-discharging process at a cooling rate of $\beta = 7$ K/min.; Figure S8: Variations of coefficient of variation (CV) against various cooling rates of $\beta = 3\text{--}7$ K/min. The long-term thermal-cycled sample was subjected to the heat-discharging process at cooling rates of $\beta = 3\text{--}7$ K/min.; Figure S9: Variations of pre-exponential factor A against temperatures for the P2 model ($\alpha = 0.1\text{--}0.50$). The as-prepared sample was subjected to the heat-discharging process at cooling rates of $\beta =$ (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7 K/min, respectively.; Figure S10: Variations of pre-exponential factor A against temperatures for the A4 model ($\alpha = 0.5\text{--}1.0$). The as-prepared sample was subjected to the heat-discharging process at cooling rates of $\beta =$ (a) 3, (b) 4, (c), (d) 6, and (e) 7 K/min, respectively.

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contributed to the collaborate investigation and data curation. All authors have read and agreed to the published version of the manuscript.

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