Effect of Cr Addition on Cu-Mn Spinel/delafossite Redox Couples for Medium-high Temperature Thermochemical Energy Storage

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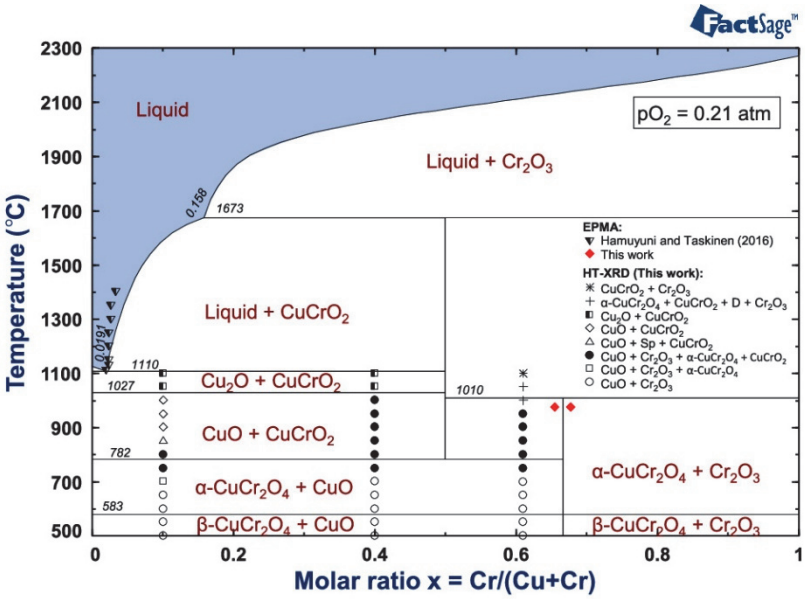

Fig.S1 Phase diagram of Cu-Cr-O (pO_2=0.21)[1]

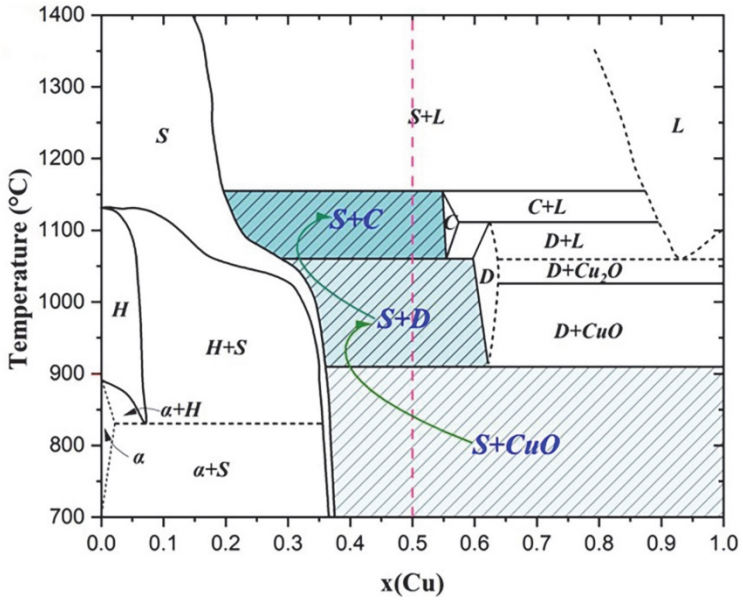

Fig.S2 Phase diagram of Cu-Mn-O (pO_2 = 0.21 atm), (H = hausmannite, S = spinel, C = crednerite, D = delafossite, α = α-Mn_2O_3)[2]

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Table S1. Some kinetic models used in the solid-state kinetics.[3]

	Reaction model	Code	$f(\alpha)$	$g(\alpha)$
1	Power law	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P2/3	$\frac{2}{3}\alpha^{-1/2}$	$\alpha^{3/2}$
5	Three-dimensional diffusion	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
6	Two-dimensional diffusion	D2	$\frac{1}{[-\ln(1-\alpha)]}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
7	One-dimensional diffusion	D1	$\frac{1}{2\alpha}$	α^2
8	Mampel (first order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
9	Avrami-Erofeev	A4	$4(1-a)[-\ln(1-a)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
10	Avrami-Erofeev	A3	$3(1-a)[-\ln(1-a)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
11	Avrami-Erofeev	A2	$2(1-a)[-\ln(1-a)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
12	Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
13	Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$

Derivation and supplementation of kinetic-related equations[4]*:*

The rate of solid-state reaction can be expressed by the following equation:

$$r = \frac{d\alpha}{dt} = Aexp\left(-\frac{E_a}{RT}\right)f(\alpha) \qquad (S1)$$

where α is the conversion rate at time t, $f(\alpha)$ is the reaction model depending on the reaction mechanism, E_a is the activation energy, A is the pre-exponential factor, and T is the absolute temperature.

The kinetic rate equation at infinite temperature is obtained by introducing the generalized time θ defined as:

$$\theta = \int_0^t \exp\left(-\frac{E_a}{RT}\right)dt \qquad (S2)$$

where θ denotes the reaction time taken to attain a particular α at infinite temperature. Differentiation of Eq.S2 leads to:

$$\frac{d\theta}{dt} = \exp\left(-\frac{E_a}{RT}\right) \qquad (S3)$$

Combining Eq.S1 and Eq.S3, the following expression is obtained:

$$\frac{d\alpha}{d\theta} = Af(\alpha) = \frac{d\alpha}{dt}\exp\left(\frac{E_a}{RT}\right) \quad (S4)$$

where dα/dθ corresponds to the generalized conversion rate, obtained by extrapolating the reaction rate in real time, dα/dt, to infinite temperature. The integrated form of the kinetic rate is obtained as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A\int_0^{\theta} d\theta = A\theta \quad (S5)$$

From the integral kinetic equation at infinite temperature in integral form, we can obtain the following equation using a reference point at α =0.5.

$$\frac{g(\alpha)}{g(0.5)} = \frac{\theta}{\theta_{0.5}} \quad (S6)$$

From the kinetic data under non-isothermal conditions, θ can be calculated by:

$$\theta = \frac{1}{\beta}\int_0^{T} \exp\left(-\frac{E_a}{RT}\right)dT = \frac{E_a}{\beta R}\int_x^{\infty} \frac{\exp(-x)}{x^2}dx = \frac{E}{\beta R}p(x)$$

where $x = E_a$/RT. The function p(x) cannot be expressed in a closed form, although several convergent series exist for its approximation. For example, the fourth rational approximation can be expressed as follows:

$$p(x) = \frac{e^{-x}}{x}\pi(x)$$

and

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}$$

For a linear heating rate, the $\theta/\theta_{0.5}$ can be calculated from the following equation:

$$\frac{\theta}{\theta_{0.5}} = \frac{p(x)}{p(x_{0.5})}$$

The knowledge of α as a function of temperature and the value of E_a is then required for calculating the experimental master plot of $\theta/\theta_{0.5}$ against α from experimental data obtained under a linear heating program.

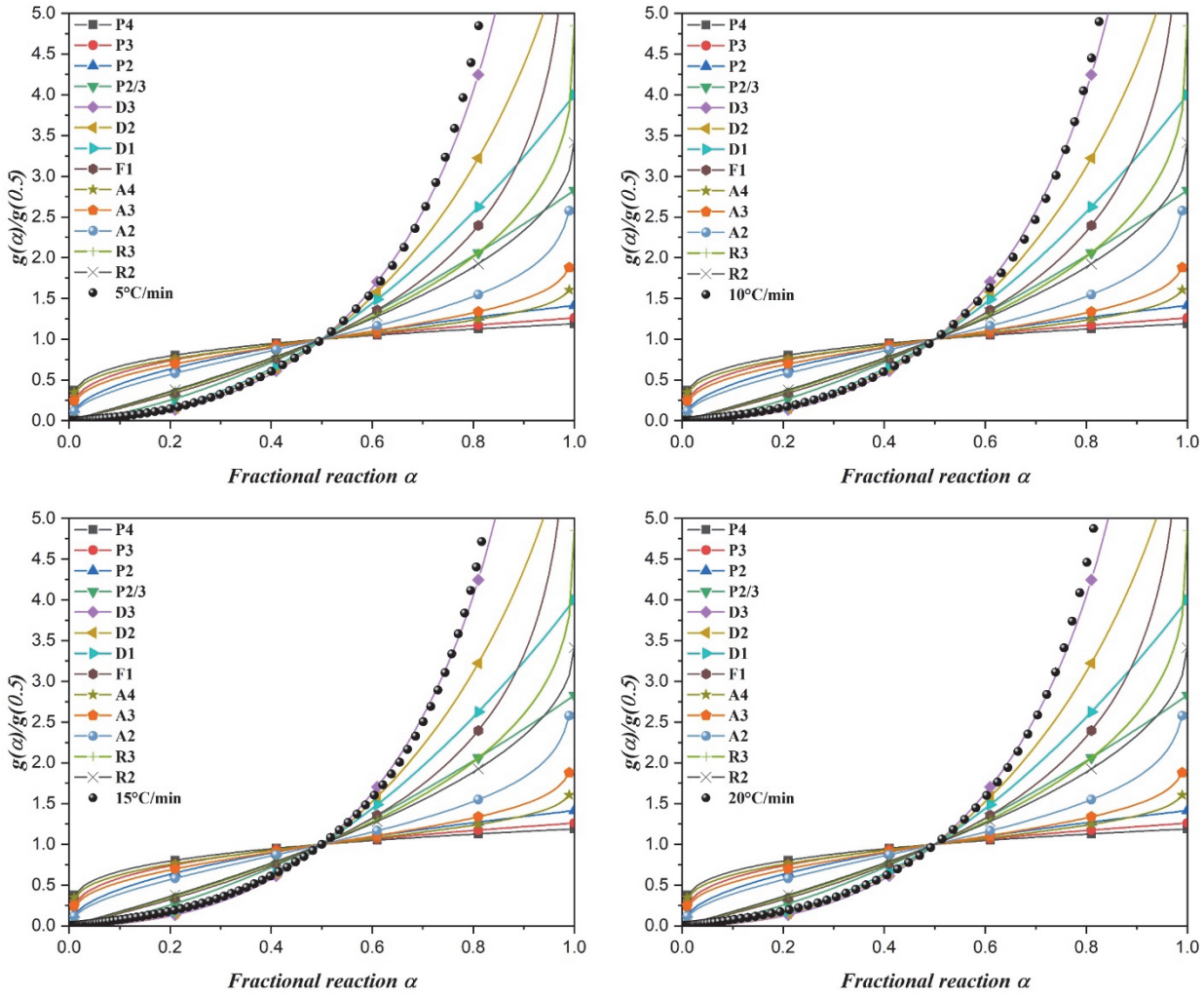

Fig.S3 g(α)/g(0.5) master plots of R-CuMn with different heating ramps (5, 10, 15, and 20 °C/min); based on the fitting results, reaction model D3 was determined

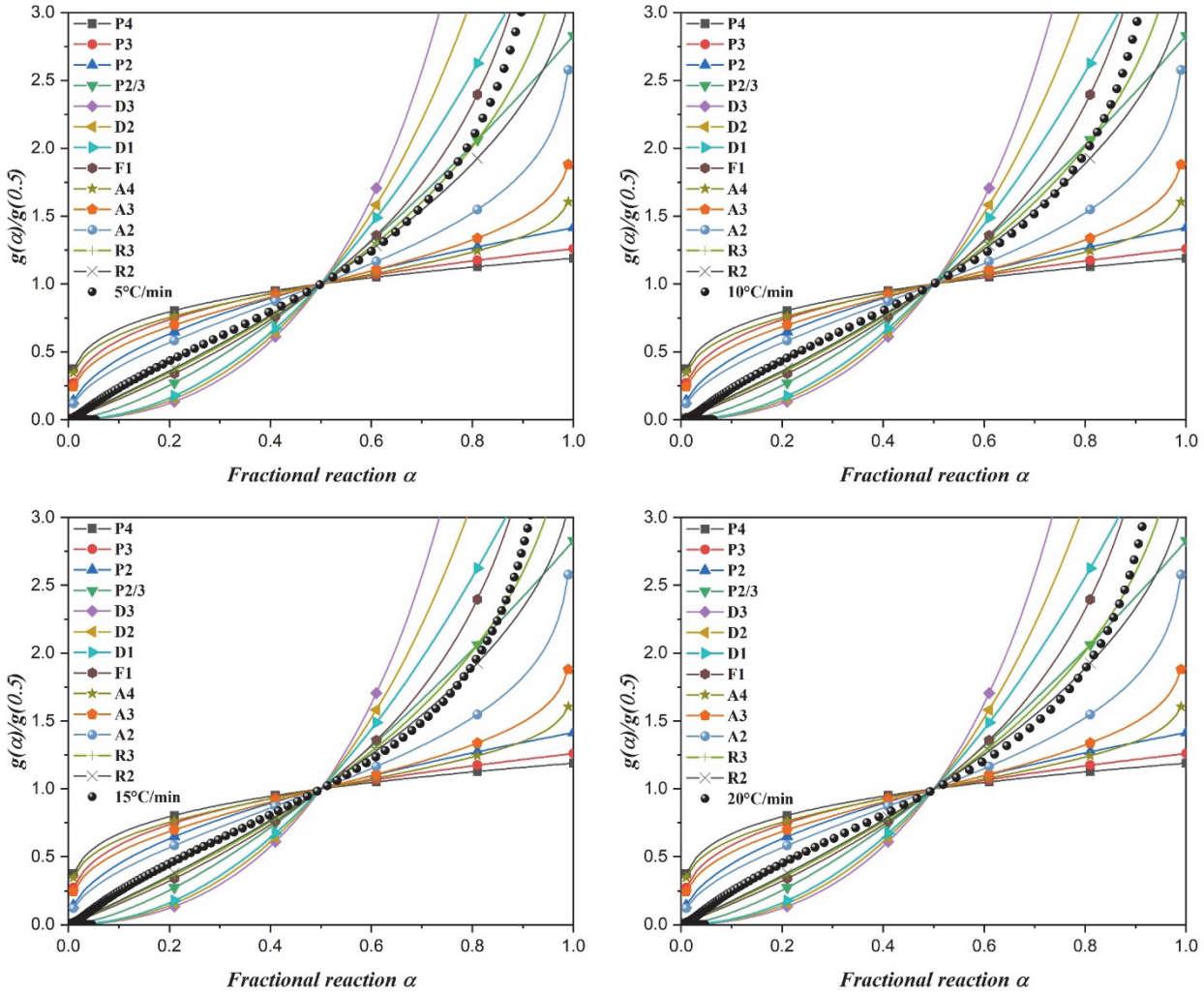

Fig.S4 g(α)/g(0.5) master plots of R-$CuCr_{0.1}Mn_{0.9}$ with different heating ramps (5, 10, 15, and 20 °C/min); based on the fitting results, reaction model R3 was determined

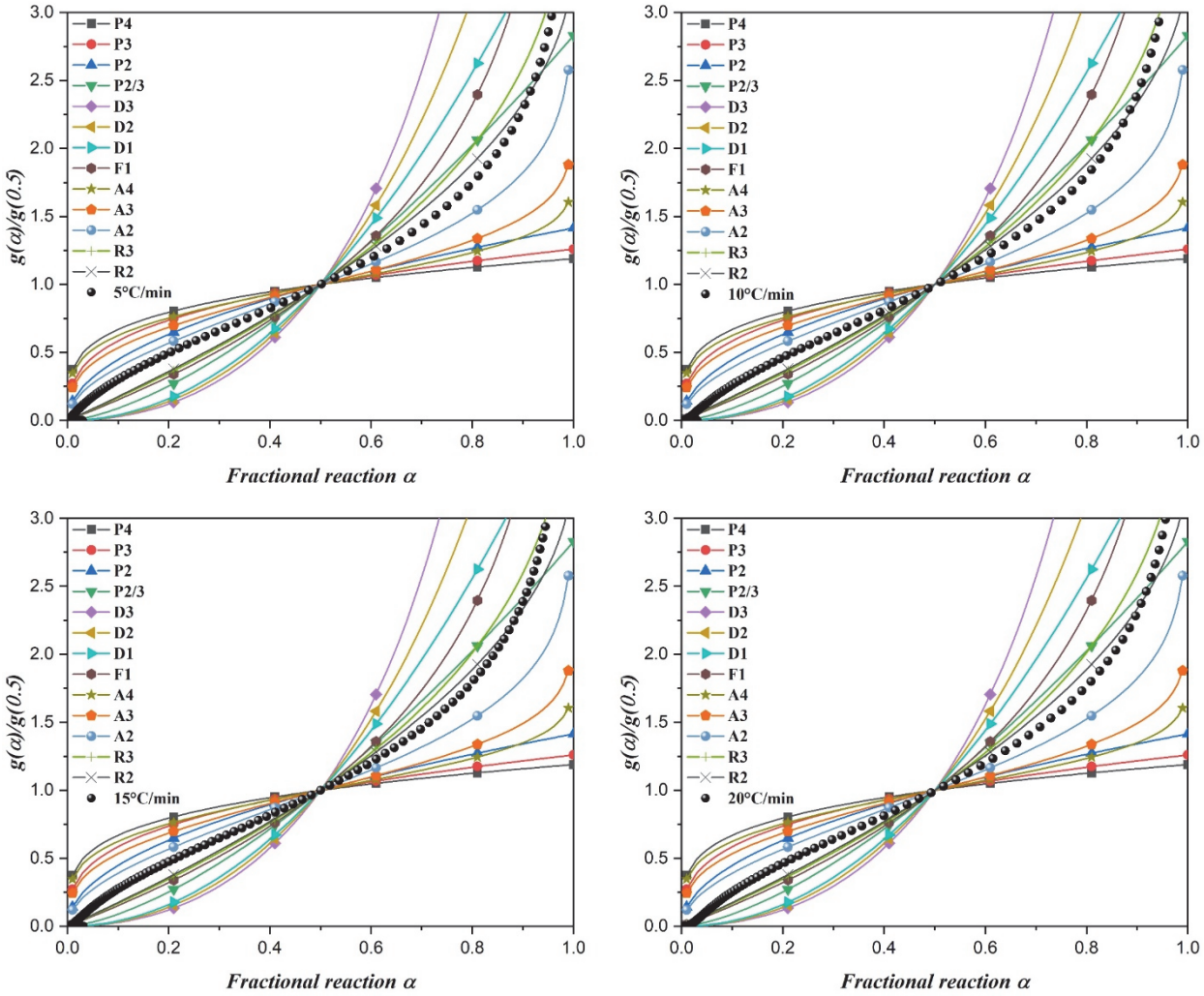

Fig.S5 g(α)/g(0.5) master plots of R-$CuCr_{0.3}Mn_{0.7}$ with different heating ramps (5, 10, 15, and 20 °C/min); based on the fitting results, reaction model R2 was determined

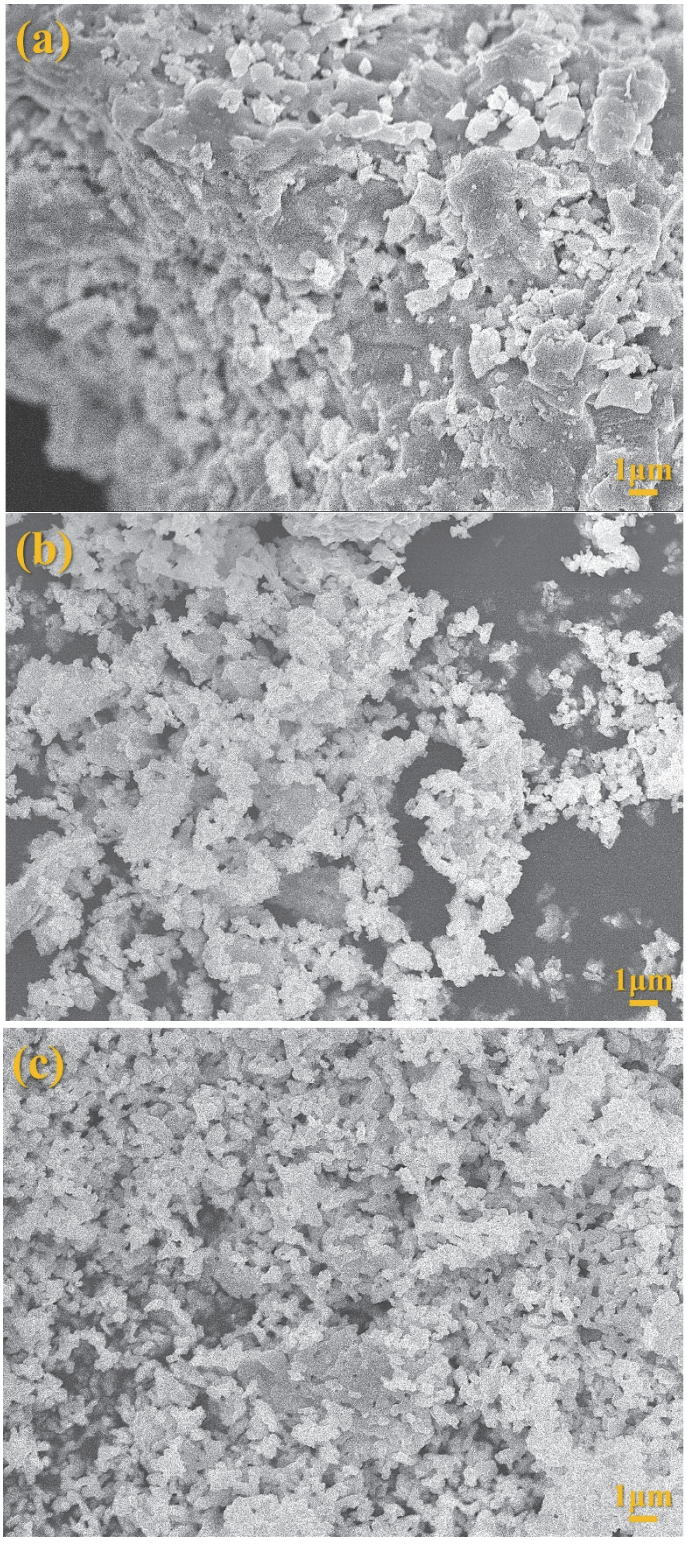

Fig.S6 SEM images of (a): R-CuMn; (b): R-$CuCr_{0.1}Mn_{0.9}$; (c): R-$CuCr_{0.3}Mn_{0.7}$

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(2) Chen, X.; Kubota, M.; Yamashita, S.; Kita, H. Exploring Cu-Based Spinel/Delafossite Couples for Thermochemical Energy Storage at Medium-High Temperature. *ACS Appl. Energy Mater.* **2021**, *4* (7), 7242–7249.

(3) Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee Recommendations for Performing Kinetic Computations on Thermal Analysis Data. *Thermochim. Acta* **2011**, *520* (1–2), 1–19.

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