

Supporting Information

Microstructure-resolved phase-field modelling reveals pore-scale controls and hydrogel design principles for hydrogen hydrate storage

Yuxuan Zhang^{a,*}, Lijin Chen^a, Ming S. Liu^b, Fei Wang^c, Praveen Linga^d, Benjapon Chalermnsinsuwan^e, Adam W. Perriman^{f,g,h}, Valeska P. Ting^{a,g,i}, Xiaolin Wang^{a,*}

^a School of Engineering, The Australian National University, Canberra, ACT 2601, Australia

^b Dimer Technologies Pty Ltd, Level 27, 101 Collins Street, Melbourne 3000, Australia

^c College of Electromechanical Engineering, Shandong Engineering Laboratory for Preparation and Application of High-performance Carbon-materials, Qingdao University of Science & Technology, Qingdao 266061, China

^d Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 117585, Singapore

^e Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^f John Curtin School of Medical Research, The Australian National University, Canberra, ACT 2601, Australia

^g Research School of Chemistry, Australian National University, Canberra, ACT 2601

^h School of Cellular and Molecular Medicine, University of Bristol, Bristol, BS8 1TD, UK

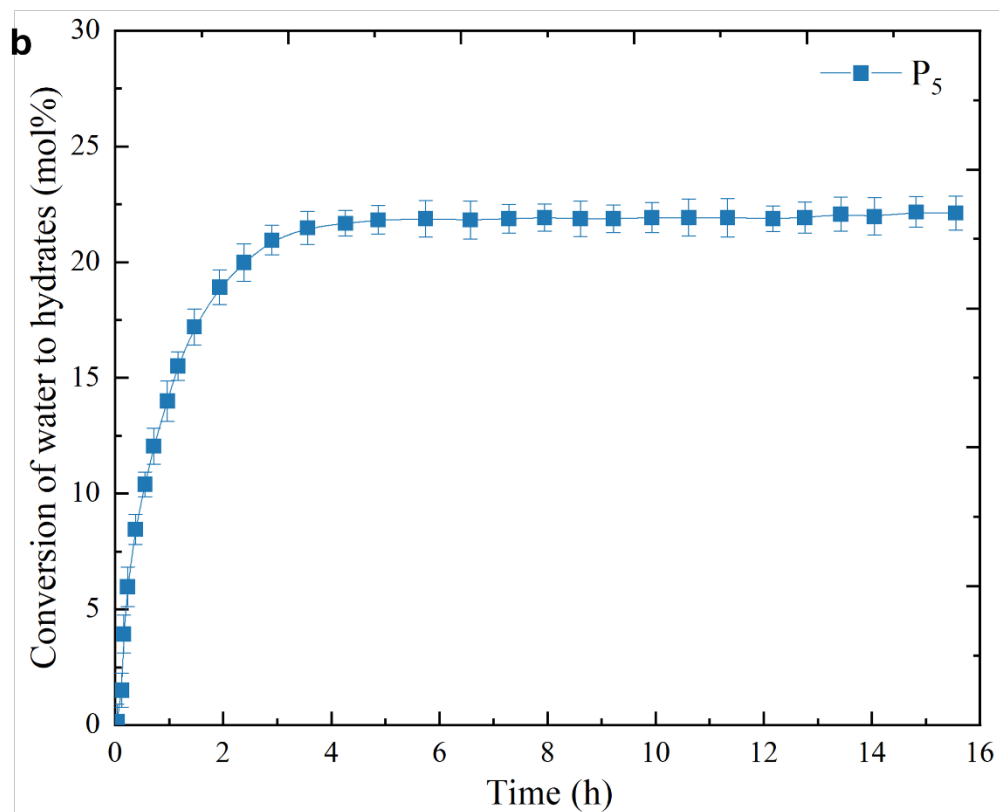
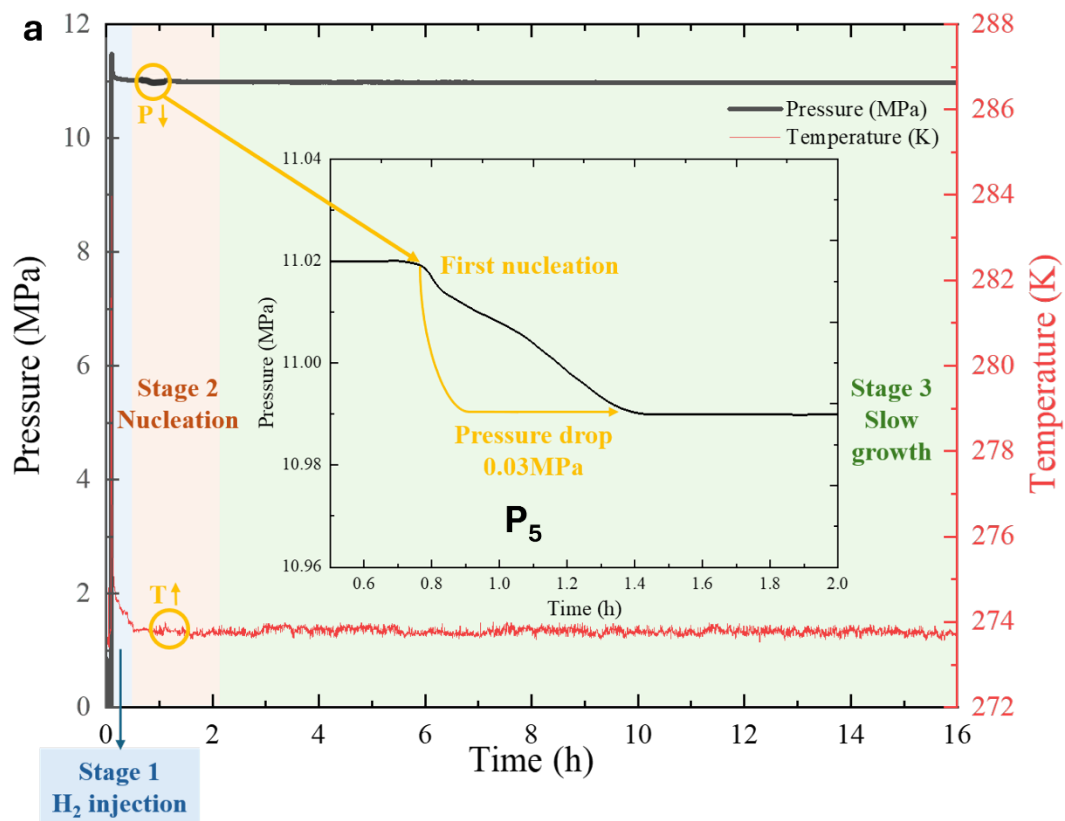
ⁱ Department of Mechanical Engineering, University of Bristol, Bristol, BS8 1TR, UK

Correspondence should be addressed to Y.Z. (Yuxuan.Zhang@anu.edu.au) or X.W. (xiaolin.wang@anu.edu.au).

Supplementary Note 1 Experimental reference data

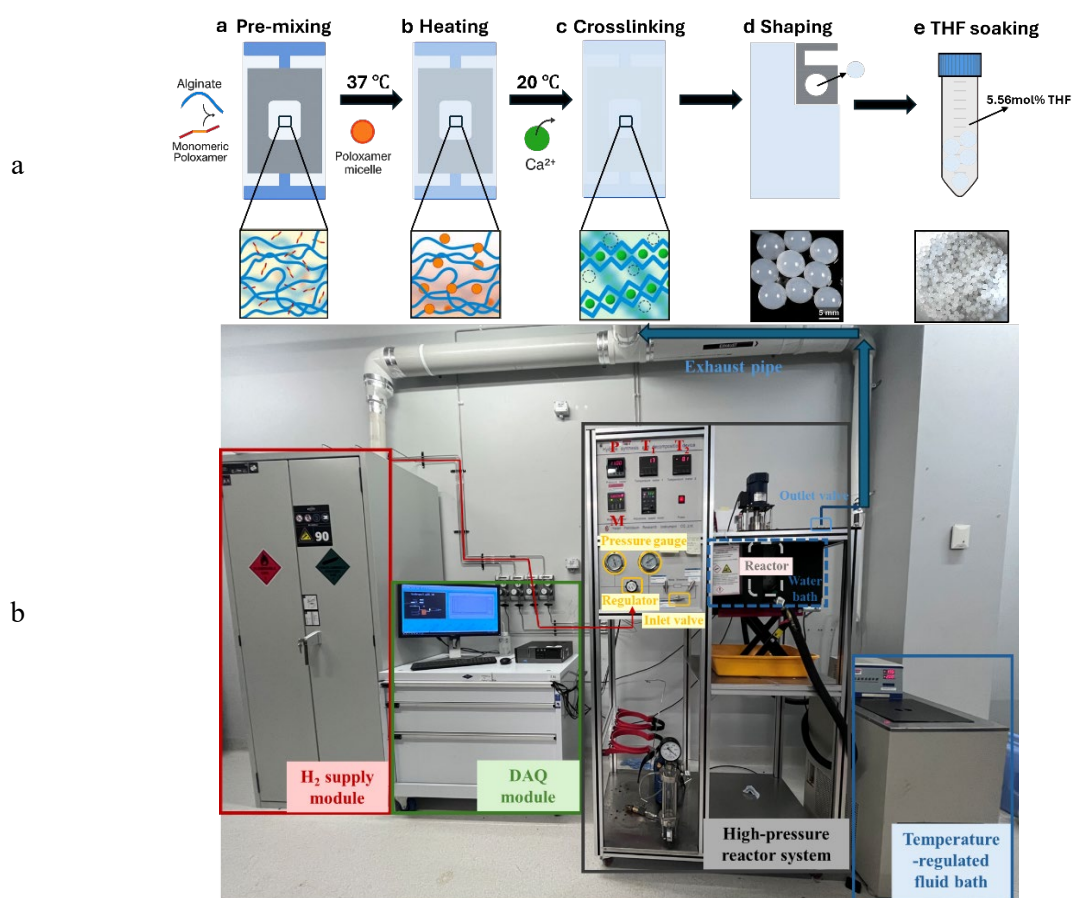
Supplementary Fig. 1a presents a representative pressure–temperature evolution during H₂–THF hydrate formation in the optimized hydrogel (P₅) under an initial pressure of 11.0 MPa and a temperature of 273.8 K. Three characteristic stages can be identified, namely H₂ charging, hydrate nucleation, and hydrate growth. Hydrate nucleation is evidenced by a distinct pressure decline occurring at approximately 0.81 h, indicating the onset of rapid hydrate formation. Thereafter, H₂ is continuously consumed as hydrate growth proceeds until the system gradually approaches equilibrium. This experimentally observed pressure evolution provides the basis for identifying the nucleation point and characterizing the H₂–THF hydrate growth process incorporated into the coupled phase-field model.

Supplementary Fig. 1b shows the corresponding evolution of water-to-hydrate conversion obtained from the same experiment. Following nucleation, H₂–THF hydrate conversion increases rapidly during the initial growth period before gradually approaching a plateau value of approximately 22%, indicating completion of hydrate formation. The experimentally measured hydrate conversion profile serves as the primary reference dataset for parameter calibration and quantitative validation of the coupled phase-field model developed in this study. Although only one representative experiment is presented here for clarity, the extracted kinetic characteristics are consistent with repeated experiments performed under identical operating conditions.

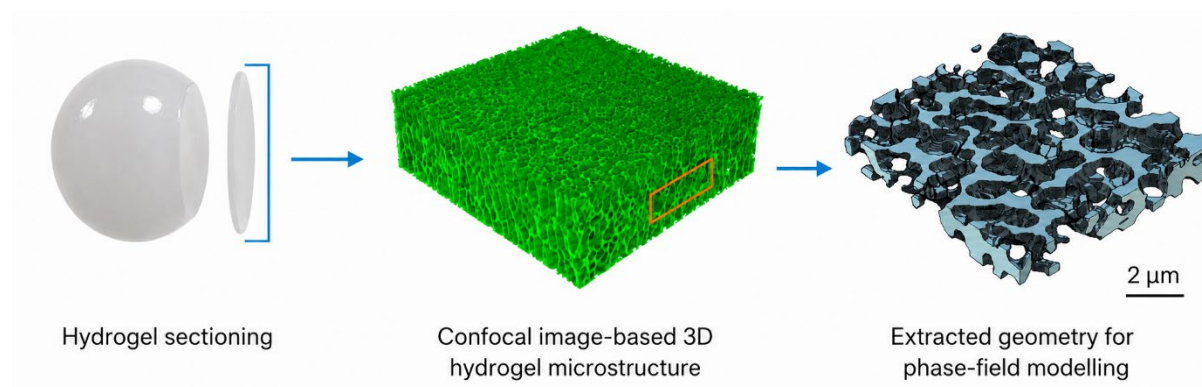


Supplementary Fig. 1. Experimental reference data for phase-field model parameterization and validation. (a) Pressure and temperature evolution during H_2 -THF hydrate formation. (b) Temporal evolution of water-to-hydrate conversion.

Supplementary Methods 1 Experimental setup and microstructure



Supplementary Fig. 2 (a) Synthesis procedures of hydrogel; (b) Experimental setup for H₂ hydrate formation.



Supplementary Fig. 3 hydrogel microstructure and the representative computational domain.

Supplementary Methods 2 Model parameterization and selection

The parameters used in the coupled phase-field model were determined using a hierarchical procedure to distinguish physically specified quantities from numerically regularizing and effective kinetic parameters. The experimental temperature, pressure, hydrogel geometry, and initial conditions were prescribed directly from the hydrate formation experiments. Thermophysical and stoichiometric parameters were obtained from established hydrate properties or calculated from the assumed H₂–THF hydrate composition. The diffuse-interface parameters were determined from the computational resolution and hydrate–liquid interfacial energy.

The numerical interface parameters were derived following the free-energy formulation used in previous pore-scale hydrate phase-field models. The diffuse-interface thickness was defined as

$$\xi_{\text{pf}} = 6\Delta x \quad (1)$$

where Δx is the characteristic spatial resolution of the computational mesh. The factor of six provides a sufficiently smooth numerical transition between the liquid and hydrate phases while retaining an interface thickness small relative to the characteristic hydrogel pore size. A similar treatment has been adopted in previous hydrate phase-field modelling, where the artificial interface was prescribed as six computational grid spacings.

The auxiliary parameter b_{pf} was calculated from

$$b_{\text{pf}} = 2 \tanh^{-1}(1 - 2\lambda_{\text{pf}}) \quad (2)$$

where $\lambda_{\text{pf}} = 0.1$ defines the phase-field interval associated with the diffuse interface. The gradient-energy coefficient and double-well barrier coefficient were then calculated as

$$\varepsilon_{\text{pf}} = \left(\frac{3\xi_{\text{pf}}\sigma_{\text{hw}}}{b_{\text{pf}}} \right)^{1/2} \quad (3)$$

and

$$w_{\text{pf}} = \frac{6b_{\text{pf}}\sigma_{\text{hw}}}{\xi_{\text{pf}}} \quad (4)$$

respectively. These definitions ensure that the prescribed diffuse interface recovers the selected hydrate–water interfacial free energy while maintaining a consistent relationship between the gradient and double-well contributions. The same functional dependence of ε_{pf} and w_{pf} on interfacial thickness and interfacial energy is used in the reference pore-scale hydrate phase-field formulation [1].

A hydrate–liquid interfacial energy of

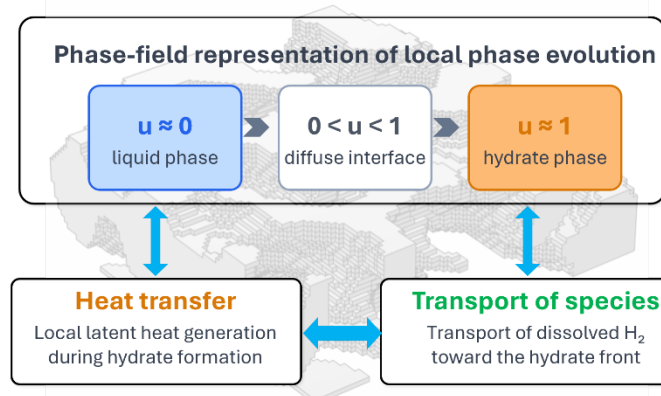
$$\sigma_{\text{hw}} = 0.025 \text{ N m}^{-1} \quad (5)$$

was adopted. This value is consistent with reported THF hydrate–water interfacial free energies of approximately $24 \pm 8 \text{ mJ m}^{-2}$ from experiment and $27 \pm 2 \text{ mJ m}^{-2}$ from molecular simulation [2].

Supplementary Table 1 Thermophysical properties of H₂-THF hydrate.

Density (g cm ⁻³) [3]	Heat capacity (J kg ⁻¹ K ⁻¹) [4]	Thermal conductivity (W m ⁻¹ K ⁻¹) [5]	Dissociation enthalpy (kJ mol ⁻¹) [6]
1.02	2500	0.5	212

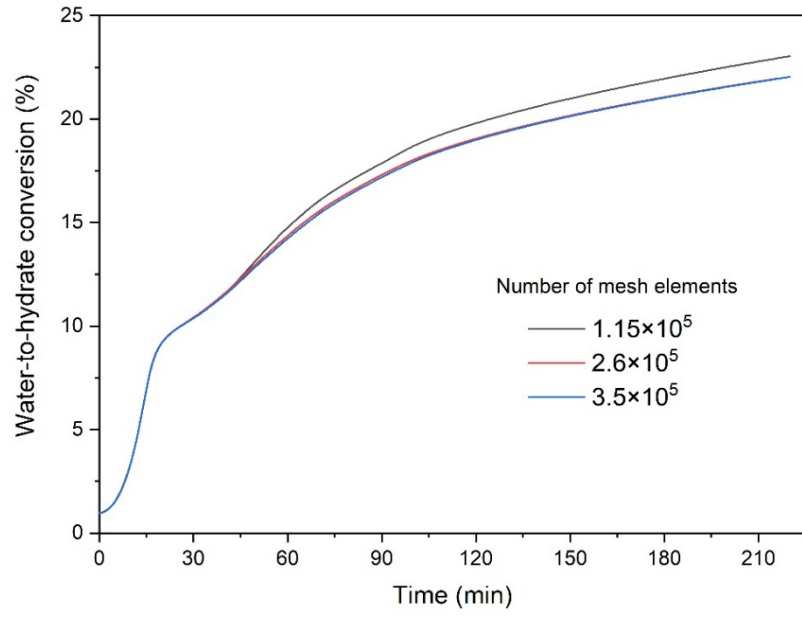
Supplementary Methods 3 Coupled modelling framework

**Supplementary Fig. 4** Schematic of the coupled phase-field, species transport, and heat transfer framework.

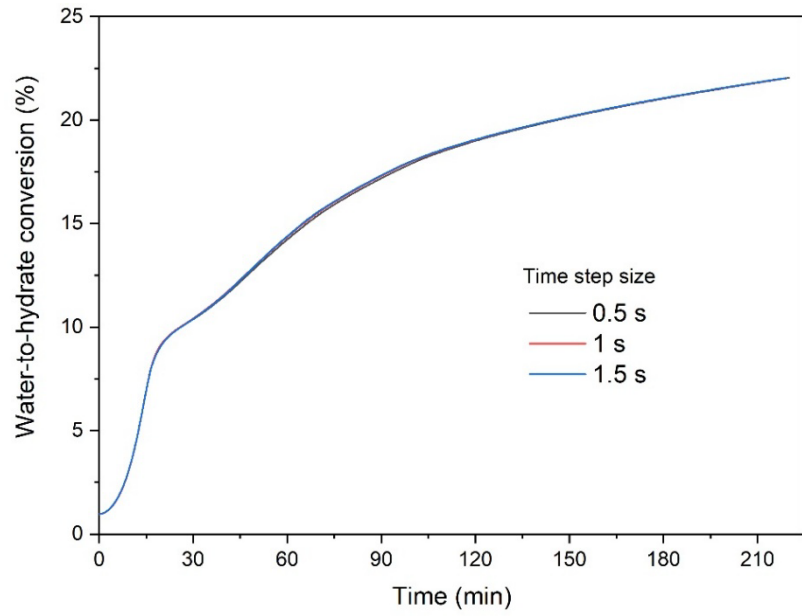
Supplementary Methods 4 Mesh and time-step independence analysis

Mesh and time step size independence analyses were performed to ensure that the predicted hydrate-conversion kinetics were not affected by the numerical resolution. For the mesh independence analysis, three computational meshes containing approximately 1.5×10^5 , 2.6×10^5 , and 3.5×10^5 elements were examined while all other model parameters and numerical settings were kept unchanged. As shown in **Supplementary Fig. 5a**, the coarse mesh produced a progressively higher water-to-hydrate conversion during the intermediate and late stages of hydrate formation. In contrast, the conversion curves obtained using 2.6×10^5 and 3.5×10^5 elements were nearly coincident throughout the simulation, indicating that further mesh refinement had a negligible influence on the predicted conversion kinetics. Therefore, the mesh containing approximately 2.6×10^5 elements was selected to balance numerical accuracy and computational efficiency.

The time-step-independence analysis was subsequently conducted using the selected mesh with time-step sizes of 0.5, 1.0, and 1.5 s. As shown in **Supplementary Fig. 5b**, the resulting water-to-hydrate conversion curves overlap closely over the entire simulation period, with no appreciable differences in either the early rapid-growth stage or the subsequent slower-growth stage. These results demonstrate that the numerical solution is insensitive to the tested time-step range. Accordingly, a time-step size of 1.0 s was adopted for all subsequent simulations.



a



b

Supplementary Fig. 5. Numerical independence analysis of the coupled phase-field model: (a) water-to-hydrate conversion predicted using meshes containing approximately 1.5×10^5 , 2.6×10^5 , and 3.5×10^5 elements; and (b) water-to-hydrate conversion predicted using time-step sizes of 0.5, 1.0, and 1.5 s.

Supplementary References

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