nature synthesis

Article

https://doi.org/10.1038/s44160-023-00479-0

Optimal thermodynamic conditions to minimize kinetic by-products in aqueous materials synthesis

In the format provided by the authors and unedited

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Supplementary Note 1.

Software: Synthesis Condition Optimizer

As described in the Results and Methods sections, we defined thermodynamic competition as the difference between the free energy of the target phase and the minimum free energy that can be achieved by combining competing phases, and proved thermodynamic competition is convex considering the linearity of a phase's thermodynamic potential in an aqueous electrochemical system[1, 2]. Thus, we can use a gradient-based method to optimize synthesis conditions by minimizing thermodynamic competition. Here, we provide the pseudocode to optimize $\Delta\Phi(Y)$ to find optimum condition Y^*, where Y is an intensive variable such as, pH, in Table S1.

Algorithm: Gradient Descent Method to minimize $\Delta\Phi(Y)$ to find thermodynamic optimal condition

Choose initial Y_0, learning rate η, and maximum step number T

For step $t = 0$ to T, do

$Y_{t+1} \leftarrow Y_t - \eta g(\Delta\Phi_t)$, where $g(\Delta\Phi_t)$ is gradient of the objective function $\Delta\Phi(Y)$ at Y_t

$\Delta\Phi_{t+1} = \Delta\Phi(Y_{t+1})$

End for

Return $Y^* = Y_T$, $\Delta\Phi^* = \Delta\Phi_T$,

where Y^* is the predicted optimal synthesis condition and $\Delta\Phi^*$ is the minimized thermodynamic competition

Table S1: The Pseudocode of gradient descent method

All of the codes used for analyzing coordination environment were based on pymatgen software and its Pourbaix diagrams module[3]. We provide code to calculate the thermodynamic competition and optimize synthesis conditions by minimizing thermodynamic competition here: https://github.com/zherenwang/synthesis_condition_optimizer

Supplementary Note 2.

Additional experiments

$Li(CH_3COO)$ (anhydrous, Sigma-Aldrich, 99.9%) was used as lithium sources for the synthesis of $LiIn(IO_3)_4$. Different amounts of lithium salts (AS1: 15 mmol $Li(CH_3COO)$, AS2: 12 mmol $Li(CH_3COO)$, AS3: 8 mmol $Li(CH_3COO)$, AS4: 5 mmol $Li(CH_3COO)$) were mixed with 0.5 mmol In_2O_3 and 8 mmol H_5IO_6. The mixture was dissolved in 10 mL water. The obtained solution was sealed in an autoclave equipped with a Teflon liner (49 mL) and heated at 200 $°C$ for 132 hours, followed by natural cooling to room temperature. The products were centrifuged, washed with water 3 times, and dried in a 70 $°C$ vacuum oven for 12 hours.

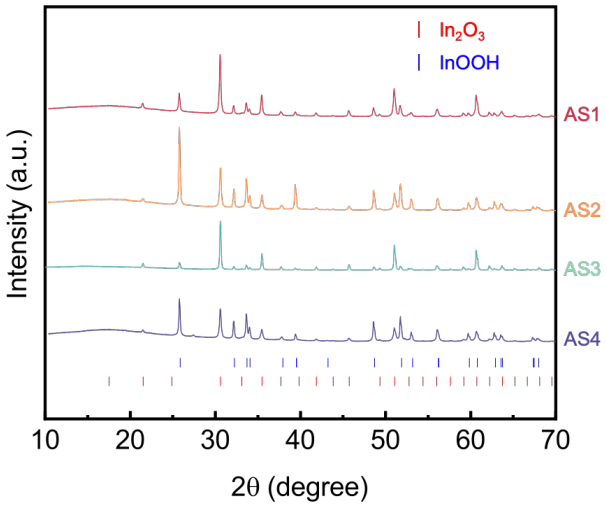

Figure S1: **XRD experimental results for addtional synthese.** AS1-AS4 are associated with varying [Li] concentration, pH.

ID	Li source	[Li]	pH	XRD results
AS1	$Li(CH_3COO)$	1.5	4.13	In_2O_3 + InOOH
AS2	$Li(CH_3COO)$	1.2	3.92	In_2O_3 + InOOH
AS3	$Li(CH_3COO)$	0.8	2.6	In_2O_3 + InOOH
AS4	$Li(CH_3COO)$	0.5	1.27	In_2O_3 + InOOH

Table S2: Synthesis parameters and XRD results for additional experiments for $LiIn(IO_3)_4$ synthesis when $Li(CH_3COO)$ was used as the only element source of [Li]. The [Li] concentrations are calculated with the assumption that all the $Li(CH_3COO)$ is completely dissociated. The specific amount of precursors can be found in the Method section. The pH values are experimentally measured.

Supplementary Note 3.

Data format of the text-mined dataset

The format of the text-mined dataset employed in Section 2.2, titled "Evaluation of MTC hypothesis from literature aqueous synthesis recipes," is illustrated in Table S3. This table includes the description of each data record, the corresponding data column names, and their respective data types.

Data description	**Data Column Name**	**Data Type**
DOI of the original paper	`doi`	*string*
Chemical formula of the product	`target`	*string*
Materials Project ID of the product	`mp_id`	*string*
Type of the product	`type`	*string*
$\Delta\Phi$ for the thermodynamic optimal conditions	`min_delta_phi (meV/atom)`	*float*
$\Delta\Phi$ for the reported text-mined synthesis conditions	`delta_phi_conditioned (meV/atom)`	*float*
$\Delta(\Delta\Phi)$	`energy_above_optimum (meV/atom)`	*float*

Table S3: Format of each data record: description, data column name, data type.

References

[1] Sun, W., Kitchaev, D. A., Kramer, D. & Ceder, G. Non-equilibrium crystallization pathways of manganese oxides in aqueous solution. *Nature Communications* **10**, 573 (2019).

[2] Boyd, S. & Vandenberghe, L. *Convex optimization* (Cambridge university press, 2004).

[3] Persson, K. A., Waldwick, B., Lazic, P. & Ceder, G. Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states. *Phys. Rev. B* **85**, 235438 (2012).