Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Preparation of battery-grade lithium carbonate by microbubble enhanced CO_2 gas-liquid reactive crystallization

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Contents

Possible chemical reactions in gas-liquid crystallization process of LiCl-$NH_3 \cdot H_2O$-CO_2 system:

$$CO_2(g) \xleftrightarrow{K_1} CO_2(aq) \quad \text{(S1)}$$

$$CO_2(aq) + 2\,H_2O \xleftrightarrow{K_2} H_3O^+ + HCO_3^- \quad \text{(S2)}$$

$$HCO_3^- + H_2O \xleftrightarrow{K_3} H_3O^+ + CO_3^{2-} \quad \text{(S3)}$$

$$NH_3 + H_2O \xleftrightarrow{K_4} NH_4^+ + OH^- \quad \text{(S4)}$$

$$OH^- + HCO_3^{2-} \xleftrightarrow{K_5} H_2O + CO_3^{2-} \quad \text{(S5)}$$

$$Li^+ + CO_3^{2-} \xleftrightarrow{K_6} Li_2CO_3(s) \quad \text{(S6)}$$

Tab. S1 Comparison of thermodynamic of Li_2CO_3 products prepared by reaction crystallization of LiCl-$NH_3 \cdot H_2O$-CO_2 and LiCl-Na_2CO_3 systems.

	Reaction (1)			Reaction (2)		
T (ºC)	K	$\Delta_rH_m^\theta$ (kJ/mol)	$\Delta_rG_m^\theta$ (kJ/mol)	K	$\Delta_rH_m^\theta$ (kJ/mol)	$\Delta_rG_m^\theta$ (kJ/mol)
0	1.995E+017	-97.784	-90.502	9.346E+003	21.820	-20.772
10	4.350E+016	-98.124	-90.228	1.307E+004	21.361	-22.322
20	1.048E+016	-98.327	-89.946	1.778E+004	21.167	-23.861
30	2.770E+015	-98.439	-89.658	2.367E+004	21.145	-25.396
40	7.960E+014	-98.490	-89.367	3.095E+004	21.232	-26.932
50	2.470E+014	-98.496	-89.076	3.986E+004	21.395	-28.473
60	8.223E+013	-98.462	-88.784	5.068E+004	21.622	-30.019
70	2.921E+013	-98.394	-88.495	6.371E+004	21.901	-31.573
80	1.101E+013	-98.296	-88.208	7.930E+004	22.221	-33.136
90	4.383E+012	-98.172	-87.924	9.782E+004	22.577	-34.709

(1) Calculation method of each ion concentration in gas-liquid reactive crystallization process

The reactive system is assumed to be in transient equilibrium. The equilibrium constants of reaction equations S2 and S3 are constant at specific temperatures, so the concentrations of CO_2, CO_3^{2-} and HCO_3^- depend on the total carbon content and pH, as shown in equation S7-S9.[1]

$$C_{CO_{2,aq}} = C_{total}(\text{carbonate})\left[\frac{K_2}{C(\text{H}^+)} + \frac{K_2K_3}{C(\text{H}^+)^2} + 1\right]^{-1} \quad \text{(S7)}$$

$$C_{HCO_{3,aq}^-} = C_{total}(\text{carbonate})\left[\frac{C(\text{H}^+)}{K_2} + \frac{K_3}{C(\text{H}^+)} + 1\right]^{-1} \quad \text{(S8)}$$

$$C_{CO_{3,aq}^{2-}} = C_{total}(\text{carbonate})\left[\frac{C(\text{H}^+)^2}{K_2K_3} + \frac{C(\text{H}^+)}{K_3} + 1\right]^{-1} \quad \text{(S9)}$$

The amount of CO_2 absorbed in the solution at a certain time can be calculated from the total inorganic carbon content (ie, C_{total} in formula S7). The content is the sum of the carbon content in the remaining solution after the Li_2CO_3 crystallization and the carbon content in the Li_2CO_3 product at the time of sampling. The crystal quality of Li_2CO_3 can be determined by the Li^+ concentration in the solution at the initial moment and sampling time. Therefore, the cumulative absorption of CO_2 can be described as:

$$C_{Li_2CO_3} = \frac{12}{6.941\times 2}\left(C\left(Li^+\right) - C_0\left(Li^+\right)\right) \quad \text{(S10)}$$

$$C_{CO_2} = \frac{44}{12}\left(C_{total} + C_{Li_2CO_3}\right) \quad \text{(S11)}$$

(2) Calculation method of supersaturation

A strict definition of relative supersaturation is described as formula S12, where C* is the saturation solubility.[2] Since Li_2CO_3 is a sparingly soluble salt and lacks the activity coefficients of Li^+ and CO_3^{2-} in multicomponent systems. To facilitate practical application, the supersaturation can be reasonably simplified as formula (S13).

$$S_a = \left(\frac{(a_{Li^+})^2(a_{CO_3^{2-}})}{K_{ap}}\right)^{1/3} \quad \text{(S12)}$$

$$S = \left(\frac{(C_{Li^+})^2 (C_{CO_3^{2-}})}{K_{sp}} \right)^{1/3} \quad \text{(S13)}$$

The supersaturation at the time of nucleation can be calculated by Equation S14. Supersolubility can be calculated by formula S15.

$$S = \frac{S_s}{C^*} \quad \text{(S14)}$$

$$S_s = \left((C_{Li^+})^2 (C_{CO_3^{2-}}) \right)^{1/3} \quad \text{(S15)}$$

(3) Calculation method of nucleation rate

The number of crystal particles detected by FBRM as a function of time. The nucleation rate can be described as:

$$J = \frac{1}{V} \frac{dN_c}{dt} \quad \text{(S16)}$$

where J is the nucleation rate (#/s·m^3), V is the solution volume (m^3), N_c is the number of particles (#/m^3), and t is the time (s).

Average nucleation rate:

$$J_1 = \frac{J(t_{ind}) + J(t_1)}{2} \quad \text{(S17)}$$

(4) Nucleation activation energy calculation

The nucleation kinetics at 20-50 ºC can be expressed by empirical kinetic equations.[3,4]

$$J = k_n S^n \quad \text{(S18)}$$

$$k_n = A e^{(-\frac{E_a}{RT})} \quad \text{(S19)}$$

$$\ln J = \ln B - \frac{E_a}{RT} \quad \text{(S20)}$$

where k_n is the kinetic constant, S is the degree of supersaturation, n is the reaction order, A is the pre-exponential factor, B is a constant, and Ea represents the nucleation activation energy.

(5) The interface can be calculated

The interfacial energy can be fitted according to the relationship between nucleation rate and supersaturation.

$$\ln J = -\frac{4\pi\gamma^3 v^2}{3k^3T^3} * \frac{1}{(\ln S)^2} + \ln A \tag{S21}$$

According to Nielsen theory, the relationship between induction period and supersaturation can be expressed as:

$$\ln t_{ind} = K + \frac{4\pi\gamma^3 v^2}{3k^3T^3(\ln S)^2} \tag{S22}$$

Therefore, the interfacial energy can also be calculated from the relationship between the induction period and the supersaturation.

(6) Growth activation energy calculation

The growth activation energy of the crystal is calculated from the relationship of growth rate to temperature, as follows:

$$\ln r_G = \ln C - \frac{E_a}{RT} \tag{S23}$$

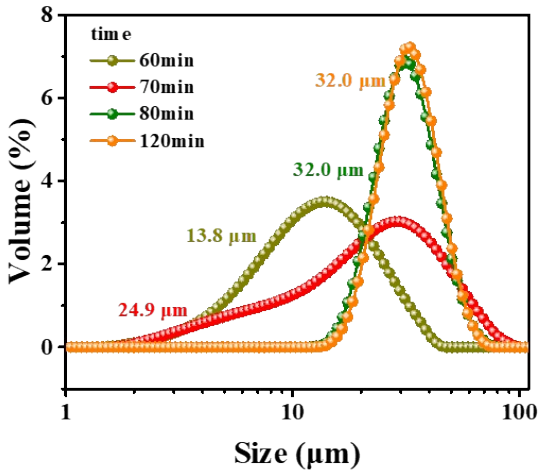

Fig. S1 Particle size distribution of Li_2CO_3 at different crystallization times under normal bubbles.

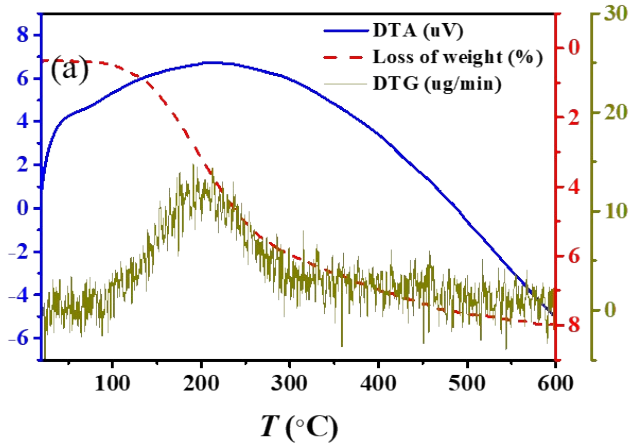

Fig. S2 Thermogravimetric analysis of Li_2CO_3 crystals.

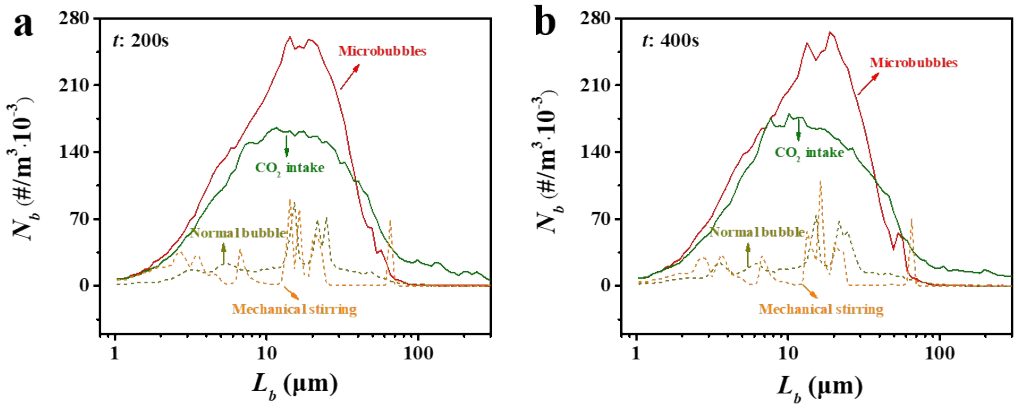

Fig. S3 The chord length distribution of Li_2CO_3 crystallization process (a) 200 s and (b) 400 s.

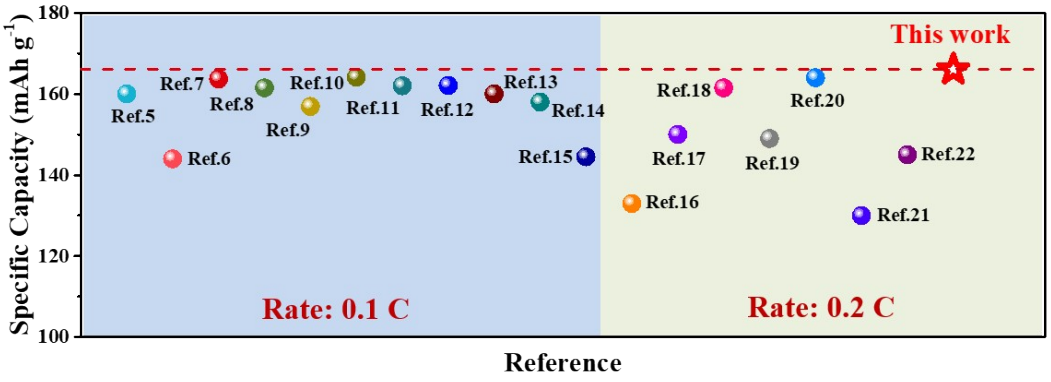

Fig. S4 Comparison of the capacities performance of the $LiFePO_4$ electrode with recently reported $LiFePO_4$-based cathodes at rates of 0.1 C and 0.2 C. The results show that the bare $LiFePO_4$ cathode prepared using the self-synthesized Li_2CO_3 as raw material exhibits superior performance.

Tab. S2 Comparison of the electrochemical performance of $LiFePO_4$ material and the

reported $LiFePO_4$-based cathodes.

Electrode Materials	0.1 C / Capacity (mA h g^{-1})	Ratio of active material	Reference
$LiFePO_4$/C	160	80%	[5]
$LiFePO_4/C_{ZIF-8}$	144	80%	[6]
$LiFePO_4$/C−B+N	163.7	80%	[7]
$LiFePO_4$/N-CNWs	161.5	80%	[8]
$LiFePO_4$/NC	156.9	80%	[9]
$LiFePO_4/B_{0.4}$-C	164.1	85%	[10]
Cl-doped $LiFePO_4$/C	162	85%	[11]
Na^+ and Cl^- co-doped $LiFePO_4$/C	162.1	75%	[12]
$LiFePO_4$/Double Carbon	160	85%	[13]
$LiFePO_4$ Nanoplate/C	158	78%	[14]
Graphene/ $LiFePO_4$	144.5	80%	[15]
Electrode Materials	**0.2 C / Capacity (mA h g^{-1})**	**Ratio of active material**	**Reference**
$LiFePO_4$/rGO	133	80%	[16]
$Zn(OAc)_2$·DEA-based $LiFePO_4$	150	80%	[17]
Mg–Ti codoped $LiFe_{0.985}Mg_{0.005}Ti_{0.01}PO_4$	161.5	88%	[18]
$LiFePO_4$/TiN	149	80%	[19]
$LiFePO_4$ nanocrystals	164	80%	[20]
$LiFePO_4$/N-GO	130	80%	[21]
$LiFePO_4$ /CNTs	145	90%	[22]
Bare $LiFePO_4$	**165.9**	**80%**	**This work**

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