Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Continuous hydrothermal leaching of $LiCoO_2$ cathode materials by using citric acid

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Detailed description of formula derivation in three-layer model.

Below are two continuity equations, Eq. S1 and S2, for the solid particles and liquid phase, respectively.

$$U_h C_h A_h + U_{mb} C_{mb} A_{mb} = U_s C_s A \quad \text{(S1)}$$

$$U_h (1 - C_h) A_h + U_{mb} (1 - C_{mb}) A_{mb} = U_s (1 - C_s) A \quad \text{(S2)}$$

Where U is the axial velocity, C is the volumetric concentration of the solid particles, and A is the pipe cross-sectional area; the subscripts h, mb, and s denote the H layer, MB layer, and the slurry, respectively; U_s is the mean velocity of the slurry; C_s is the slurry input concentration; A_h and A_{mb} are the cross-sectional areas occupied by the H and MB layer, respectively.

1) Force balance equation

For the H layer, the heterogeneous mixture is considered as a pseudoliquid with effective properties, under the shear stresses acting on the contact surface of the pipe wall with the H layer and the interface between the H and MB layers. The equation of the force balance is:

$$A_h \frac{dP}{dx} = -\tau_h S_h - \tau_{\mathrm{hmb}} S_{\mathrm{hmb}} \quad \text{(S3)}$$

Where dP/dx is the pressure drop, S_{hmb} is the interface between the H and MB layers; τ_h and τ_{hmb} are the upper layer shear stress and the interfacial shear stress acting on the perimeters S_h and S_{hmb}, respectively.

The shear stress at the pipe circumference is:

$$\tau_h = \frac{1}{2} \rho_h {U_h}^2 f_h \quad \text{(S4)}$$

And the shear stress at the interface between the H and MB layers is:

$$\tau_{\mathrm{hmb}} = \frac{1}{2} \rho_h \left(U_h - U_{\mathrm{mb}}\right)^2 f_{\mathrm{hmb}} \quad \text{(S5)}$$

Where ρ_h is the effective density of the H layer, evaluated as

$$\rho_h = \rho_s C_h + \rho_L (1 - C_h) \quad \text{(S6)}$$

Where $\rho_{S \text{ and }} \rho_L$ are the densities of the solid particles and the liquid, respectively.

The friction coefficient (f_h) at the pipe wall is found from

$$f_h = \alpha_h Re_h^{-\beta_h} \qquad \text{(S7)}$$

Where $\alpha_h = 0.046$, $\beta_h = 0.02$ for turbulent flow and $\alpha_h = 16$, $\beta_h = 1$ for laminar flow. The Reynolds number Re_h is based on the hydraulic diameter D_h, shown as the below Eq. S8 and Eq. S9.

$$Re_h = \frac{\rho_h U_h D_h}{\mu_h} \qquad \text{(S8)}$$

$$D_h = \frac{4A_h}{S_h + S_{\text{mb}}} \qquad \text{(S9)}$$

The friction coefficient at the interface (f_{nmb}) is found from

$$\frac{1}{\sqrt{2f_{\text{hmb}}}} = -0.86\ln\left(\frac{\frac{d_p}{D}}{3.7} + \frac{2.51}{Re_h\sqrt{2f_{\text{hmb}}}}\right) \qquad \text{(S10)}$$

where D and d_p are the diameters of the pipe and the particles flowing in the pipe. Here, the roughness of the interface is assumed of the order of a particle diameter.

For the MB layer, the positive force is the shear stress at the interface with the H layer, and the negative force is the dry friction force acting at the interface with the pipe wall and SB layer. The equation of the force balance is:

$$A_{\text{mb}}\frac{dP}{dx} = -F_{\text{mbsb}} - \tau_{\text{mbsb}}S_{\text{mbsb}} - F_{\text{mb}} - \tau_{\text{mb}}S_{\text{mb}} + \tau_{\text{hmb}}S_{\text{hmb}} \qquad \text{(S11)}$$

Where F_{mbsb} is the dry friction force acting at the interface between the MB and SB layers; τ_{mbsb} is the hydrodynamic shear stress acting on the interface between the MB and SB layers, S_{mbsb}; F_{mb} is the dry friction force acting at the contact surface of the MB layer with the pipe wall, S_{mb}, and τ_{mb} is the hydrodynamic shear acting on that surface.

τ_{mb} and τ_{mbsb} are expressed by

$$\tau_{\text{mb}} = \frac{1}{2}\rho_L U_{\text{mb}}^2 f_{\text{mb}} \qquad \text{(S12)}$$

$$\tau_{\text{mbsb}} = \frac{1}{2}\rho_L U_{\text{mb}}^2 f_{\text{mbsb}} \qquad \text{(S13)}$$

The friction coefficient at the pipe wall, f_{mb}, is evaluated in a similar way to f_h.

$$f_{mb} = \alpha_{mb} Re_{mb}^{-\beta_{mb}} \quad \text{(S14)}$$

where $\alpha_{mb} = 0.046$, $\beta_{mb} = 0.02$ for turbulent flow and $\alpha_{mb} = 16$, $\beta_{mb} = 1$ for laminar flow. The Reynolds number Re_{mb} is based on the hydraulic diameter D_{mb}, shown as the below Eq. S15 and Eq. S16.

$$Re_{mb} = \frac{\rho_L U_{mb} D_{mb}}{\mu_h} \quad \text{(S15)}$$

$$D_{mb} = \frac{4A_{mb}}{S_{mb} + S_{mbsb}} \quad \text{(S16)}$$

The friction coefficient at the interface between the MB and SB layers, f_{mbsb}, is evaluated similarly to f_{hmb}.

$$\frac{1}{\sqrt{2f_{mbsb}}} = -0.86 \ln\left(\frac{\frac{d_p}{D}}{3.7} + \frac{2.51}{Re_{mb}\sqrt{2f_{mbsb}}} \right) \quad \text{(S17)}$$

Here, F_{mb}, the dry friction force at the pipe wall contributed by the solid particles in the MB layer, is composed of the effect of the submerged weight of the particles, F_{Wmb}, and the transmission of stress from the interface, $F_{\phi mb}$:

$$F_{mb} = F_{Wmb} + F_{\phi mb} \quad \text{(S18)}$$

F_{Wmb} and $F_{\phi mb}$ are calculated as the below equations.

$$F_{Wmb} = 2\eta \int_{\theta_{sb}}^{\theta_{mb} + \theta_{sb}} (\rho_s - \rho_L) g C_{mb} \left(\frac{D}{2}\right)^2 \left\{ \left[\frac{2(y_{sb} - y_{mb})}{D} - 1 \right] - \sin\gamma \right\} d\gamma \quad \text{(S19)}$$

$$F_{\phi mb} = \eta \frac{\tau_{hmb} S_{mb}}{\tan(\phi)} \quad \text{(S20)}$$

Where η is the dry dynamic friction coefficient, g is the gravitational acceleration, D is the pipe diameter, y_{mb} is the height of the MB layer, y_{sb} is the height of the SB layer and θ_{mb} and θ_{sb} are the central angles associated with them, respectively. The shear stress at the interface S_{hmb} is associated with a normal stress, $\tau_N = \tau_{hmb}/\tan(\phi)$, where $\tan(\phi)$ is the tangent of the angle of internal friction.

F_{mbsb}, the contribution of the solid particle to the friction force acting on the interface S_{mbsb}, is found in a similar manner,

$$F_{\text{mbsb}} = F_{\text{Wmbsb}} + F_{\phi\text{mbsb}} \quad \text{(S21)}$$

Where F_{Wmbsb} and $F_{\phi\text{mbsb}}$ are calculated as:

$$F_{\text{Wmbsb}} = \eta(\rho_s - \rho_L)gC_{\text{mb}}y_{\text{mb}}S_{\text{mbsb}} \quad \text{(S22)}$$

$$F_{\phi\text{mbsb}} = \eta\frac{\tau_{\text{hmb}}S_{\text{mbsb}}}{\tan(\phi)} \quad \text{(S23)}$$

For the SB layer, since it does not move, the sum of shear and frictional forces from the MB layer is less than the frictional force with the pipe wall. The equation of force balance is shown as follows.

$$A_{\text{sb}}\frac{dP}{dx} + F_{\text{mbsb}} + \tau_{\text{mbsb}}S_{\text{mbsb}} \le F_{\text{sb}} \quad \text{(S24)}$$

Where A_{sb} is the cross-sectional area of the SB layer, F_{sb} is the dry friction force acting on the periphery of the SB layer, S_{sb}. F_{sb} is evaluated in a similar way to F_{mb}:

$$F_{sb} = F_{Wab} + F_{\phi sb} \quad \text{(S25)}$$

F_{Wsb} and $F_{\phi\text{sb}}$ are calculated as:

$$F_{\text{Wsb}} = 2\eta_s\int_{-\frac{\pi}{2}}^{\theta_{\text{sb}}} (\rho_s - \rho_L)gC_{\text{sb}}\left(\frac{D}{2}\right)^2\left\{\left[\frac{2y_{\text{sb}}}{D} - 1\right] - \sin\gamma\right\}d\gamma \quad \text{(S26)}$$

$$F_{\phi\text{sb}} = \eta_s\frac{\tau_{\text{hmb}}S_{\text{sb}}}{\tan(\phi)} \quad \text{(S27)}$$

Where η_s is the dry static friction coefficient and C_{sb} is the concentration of the SB layer.

2) Diffusion

The dispersion of the solid particles in the H layer is assumed to be evaluated by the below diffusion equation.

$$\varepsilon\frac{d^2C}{dy^2} + w\frac{dC}{dy} = 0 \quad \text{(S28)}$$

where y is the vertical coordinate, perpendicular to the pipe axis, ε is the diffusion coefficient, and w is the terminal settling velocity of the particles. Lateral variations of the concentration are neglected, and the concentration distribution is assumed one-dimensional. Taking the concentration of the MB layer, C_{mb}, as the boundary condition, the concentration profile in the H layer is obtained:

$$C(y) = C_{\mathrm{mb}}\exp\left(-\frac{w\left[y-\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)\right]}{\varepsilon}\right) \tag{S29}$$

Where w and ε are calculated in the same way as the previous report.[1] Upon integration over the cross section of the upper layer, the equation for the mean concentration in that layer, C_{h}, is obtained:

$$\frac{C_h}{C_{\mathrm{mb}}} = \frac{2\left(\frac{D}{2}\right)^2}{A_h}\int_{\theta_{\mathrm{mb}}+\theta_{\mathrm{sb}}}^{\pi/2} exp\left\{-\frac{wD}{2\varepsilon}\left[\sin\gamma - \sin\left(\theta_{\mathrm{mb}}+\theta_{\mathrm{sb}}\right)\right]\right\}\cos^2\gamma d\gamma \tag{S30}$$

All the geometrical properties which appear in the above equations can be expressed in terms of y_{mb} and y_{sb} for a given pipe diameter, D:

$$A_h = \left(\frac{D}{2}\right)^2\left\{\cos^{-1}\left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right] - \left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right]\sqrt{1-\left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right]^2}\right\} \tag{S31}$$

$$A_{\mathrm{sb}} = \left(\frac{D}{2}\right)^2\left\{\pi - \cos^{-1}\left(\frac{2y_{\mathrm{sb}}}{D}-1\right) + \left(\frac{2y_{\mathrm{sb}}}{D}-1\right)\sqrt{1-\left(\frac{2y_{\mathrm{sb}}}{D}-1\right)^2}\right\} \tag{S32}$$

$$A_{\mathrm{mb}} = \frac{1}{4}\pi D^2 - \left(A_h + A_{\mathrm{sb}}\right) \tag{S33}$$

$$S_h = D\cos^{-1}\left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right] \tag{S34}$$

$$S_{\mathrm{sb}} = D\left[\pi - \cos^{-1}\left(\frac{2y_{\mathrm{sb}}}{D}-1\right)\right] \tag{S35}$$

$$S_{\mathrm{mb}} = \pi D - \left(S_h + S_{\mathrm{sb}}\right) \tag{S36}$$

$$S_{\mathrm{hmb}} = D\sqrt{1-\left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right]^2} \tag{S37}$$

$$S_{\mathrm{mbsb}} = D\sqrt{1-\left(\frac{2y_{\mathrm{sb}}}{D}-1\right)^2} \tag{S38}$$

$$\theta_{\mathrm{mb}} = \cos^{-1}\left(\frac{2y_{\mathrm{sb}}}{D}-1\right) - \cos^{-1}\left[\frac{2\left(y_{\mathrm{mb}}+y_{\mathrm{sb}}\right)}{D}-1\right] \tag{S39}$$

$$\theta_{\mathrm{sb}} = \frac{\pi}{2} - \cos^{-1}\left(\frac{2y_{\mathrm{sb}}}{D}-1\right) \tag{S40}$$

3) Flow pattern map

Here, the purpose to apply the three-layer model is to search for the conditions under which the slurry can be conveyed without depositing in the pipe. Therefore, in this study, the formation of the SB layer was not considered to simplify the calculation method, and the calculation was limited to the condition that the MB layer was the minimum (y_{mb} = dp, y_{sb} = 0).

After substituting the initial condition (y_{mb} = dp, y_{sb} = 0) to Eq. (S30-S40) numerically, Eq. (S1-S2) can be derived, and the below equation can be obtained.

$$U_h = U_s \frac{A}{A_{mb}} \frac{C_s - C_{mb}}{C_h - C_{mb}} \qquad \text{(S41)}$$

From Eq. (S3-S41), the maximum flow velocity (U_h) at which the MB layer is formed at a certain pulp density (C_s) can be obtained. The boundary between the H and MB layers can be changed by changing C_s. A flow pattern map, which expresses the relationship between C_s and U_h, was constructed and used to predict the flow state of the slurry and set the conditions under which accumulation or deposition does not occur.

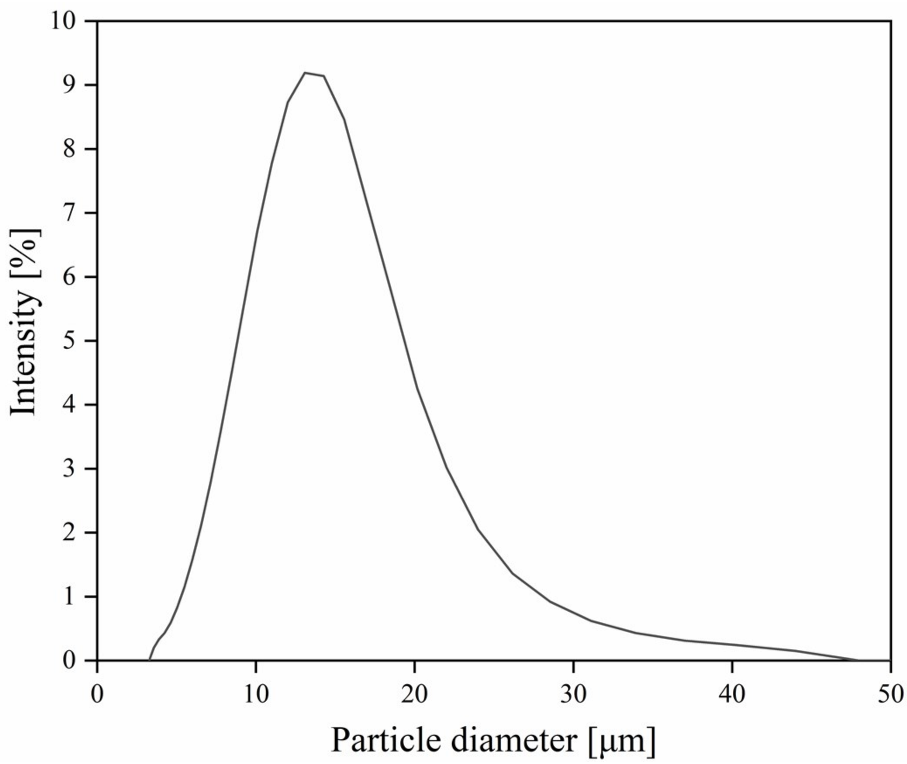

Fig. S1 The size distribution of $LiCoO_2$ particles.

Reference:

1. P. Doron, D. Granica and D. Barnea, *Int. J. Multiphase Flow*, 1987, **13**, 535-547.