Supplementary Information

Oxidation-Resistant Micron-Sized Cu-Sn Solid Particles Fabricated by a One-Step and Scalable Method

Yujia Liang, a Su Cheun Oh, a Xizheng Wang, c Howard Glicksman, b Dongxia Liu, a Sheryl Ehrman a *

a Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States
b DuPont Electronic Technologies, Research Triangle Park, North Carolina 27709, United States
c Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

* e-mail: sehrman@umd.edu

Contents

1. Additional morphology and structure characterization of CuSn, particles ....................................... 2
2. Additional results of oxidation behavior of CuSn, particles ................................................................. 7
3. Theoretical analysis of particle oxidation ................................................................................................ 15
   a) Shrinking-core model simulation ........................................................................................................ 15
   b) Detailed procedures to obtain the D_e .................................................................................................. 17
4. References for Electronic Supplementary Information .................................................................... 24

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1. Additional morphology and structure characterization of CuSn$_y$ particles

Fig. S1 SEM images with the corresponding high magnification images of the areas marked by dashed boxes of CuSn$_{0.2}$ (a), CuSn$_{0.4}$ (b), CuSn$_{0.8}$ (c), and CuSn (d). The scale bars in all images are 1 μm.
Fig. S2 TEM images of CuSn$_{0.05}$ (a), CuSn$_{0.1}$ (b), CuSn$_{0.2}$ (c), CuSn$_{0.4}$ (d), CuSn$_{0.8}$ (e), and CuSn (f) products.
Fig. S3 Line scans of Cu and Sn elemental profiles of CuSn$_{0.05}$ (a), CuSn$_{0.1}$ (b), CuSn$_{0.2}$ (c), CuSn$_{0.4}$ (d), and CuSn$_{0.8}$ (e).
**Fig. S4** XPS signals of Cu (a-c), CuSn$_{0.01}$ (d-f), CuSn$_{0.05}$ (g-i), CuSn$_{0.1}$ (j-l), CuSn$_{0.2}$ (m-o), CuSn$_{0.4}$ (p-r), CuSn$_{0.8}$ (s-u), and CuSn (v-x) particles before and after sputtering. Images in the left column represent the spectra from Sn 3d electrons. Images in the middle column illustrate the spectra from Cu 2p electrons. Images in the right column are the spectra from Cu LMM Auger electrons. For Cu 2p electrons, metallic copper has a major peak at 932.4 eV.\textsuperscript{1} For Cu LMM Auger electrons, shoulder peaks around 565 eV are attributed to metallic copper, while peaks around 570 eV are evidence for the existence of copper oxides.\textsuperscript{1,2}
2. Additional results of oxidation behavior of CuSn$_y$ particles

Fig. S5 TEM images of the Cu (a-b) and CuSn$_{0.1}$ (c-d) particles after being oxidized in ambient for 60 min at 100 °C. Oxide layers were formed on the particle surfaces as shown by the lattice fringe in (d), which is attributed to the (110) plane of Cu$_2$O (PDF No. 01-071-3645). Similar results have also been observed by other researchers in the oxidation of Cu particles.
Fig. S6 *In-situ* XRD measurements of pure Cu (a), CuSn$_{0.05}$ (b), and CuSn$_{0.1}$ (c) when the sample temperature was held at 200 °C in ambient air subject to heating. (d) The temperature profile of the sample during the oxidation. In (d), the red dots correspond to initiation of XRD scans.
Fig. S7 $O_2$ partial pressures in the product streams of the packed-bed reactor when the volume percents of $O_2$ in feed stream are 1.4% (a) and 10% (b).
Fig. S8 TEM images of Cu (a)-(b), CuSn_{0.05} (c)-(d), and CuSn_{0.1} (e)-(f) particles after being oxidized in packed-bed reactor under 300 °C. The volume percent of O_2 in feed stream is 1.4 %. (b), (d), and (f) are the higher magnification images of the areas marked by red boxes in (a), (c), and (e), respectively.
Fig. S9 TEM images of Cu (a)-(c), CuSn$_{0.05}$ (d)-(f), and CuSn$_{0.1}$ (g)-(i) particles after being oxidized in packed-bed reactor under 500 °C. The volume percent of O$_2$ in feed stream is 1.4 %. (b), (e), and (h) are the higher magnification images of the areas marked by red boxes in (a), (d), and (g), respectively. (c), (f), and (i) are the selected area electron diffraction (SAED) patterns of areas highlighted by yellow boxes in (b), (e), and (h), respectively. SAED images are obtained by performing the fast Fourier transform (FFT). The identified phases are CuO (PDF No. 01-073-6023) and SnO$_2$ (PDF No. 01-072-1147).
Fig. S10 (a) O$_2$ flow rate in the product stream of the packed-bed reactor when the volume percent of O$_2$ in feed stream is 10 %. (b) The relative weight gains of the powder during the oxidation. The weight gain is calculated by applying the trapezoidal method on the results shown in (a). (c) XRD pattern of powders after being oxidized in a packed-bed reactor at 500 °C under 10 vol % O$_2$ stream.
Fig. S11 TGA (left axis) and DSC (right axis) measurements on Cu particles (black curves) and CuSn$_{0.1}$ particles (green curves). The initial oxidation temperature of CuSn$_{0.1}$ (vertical green dashed line) is ~ 44 °C higher than Cu (black dashed line). There are two distinct exotherms in both heat flow curves at 380 °C (Cu) and 365 ºC (CuSn0.1) corresponding to the weight losses.
Fig. S12 SEM images of particles after being oxidized in a packed-bed reactor under 300 °C (a)-(c) and 500 °C (d)-(f). The volume percent of O\textsubscript{2} in the feed stream is 1.4 %. The scale bars in SEM images are 2 μm.
3. Theoretical analysis of particle oxidation

a) Shrinking-core model simulation

To test this hypothesis, the shrinking-core model (SCM) was utilized to simulate the oxidation process and to investigate the chemical kinetics and material transport.\textsuperscript{4,5} The densities of Cu (8.9 g/cm\textsuperscript{3}) and Sn (7.3 g/cm\textsuperscript{3}) are comparable to their corresponding oxides, such as Cu\textsubscript{2}O (6.0 g/cm\textsuperscript{3}), CuO (6.3 g/cm\textsuperscript{3}), SnO (6.5 g/cm\textsuperscript{3}), and SnO\textsubscript{2} (7.0 g/cm\textsuperscript{3}).\textsuperscript{6}

The particle diameter was assumed to be constant during the oxidation process at 300 °C, which is also validated by the SEM images of the post-oxidation particles, as shown in Fig. S12a-c. For oxidation at 500 °C, SCM is not applicable because of significant coagulation between particles and the resulting particle size change (Fig. S12d-f). The oxidation process can be divided into three steps: (i) migration of O\textsubscript{2} gas through the gas film around the particle to the particle surface; (ii) diffusion of O\textsubscript{2} gas through the porous oxide ash layer to the inner metal core; (iii) reaction of O\textsubscript{2} gas with metal core.\textsuperscript{4,5} If Step (i) controls the process the radius of the unreacted core, \( r_c \), can be related to the oxidation time through:\textsuperscript{4}

\[
t = \frac{\rho_p R^3}{3b k_g C_{O2,g}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad (S1)
\]

\[
\tau = \frac{\rho_p R^2}{3b k_g C_{O2,g}} \quad (S2)
\]

where \( t \) is the oxidation time. \( \tau \) is the time for a complete oxidation. \( \rho_p \) is the density of the particle. \( R \) is the radius of the particle, which is assumed to be 355 nm. \( b \) is the stoichiometric coefficient in the oxidation. \( k_g \) is the mass transfer coefficient. \( C_{O2,g} \) is the O\textsubscript{2} gas concentration in the main stream.

If Step (ii) controls the process:\textsuperscript{4}

\[
t = \frac{\rho_p R^2}{6b D_e C_{O2,g}} \left[ 1 - 3 \left( \frac{r_c}{R} \right)^2 + 2 \left( \frac{r_c}{R} \right)^3 \right] \quad (S3)
\]

\[
\tau = \frac{\rho_p R^2}{6b D_e C_{O2,g}} \quad (S4)
\]

where \( D_e \) is the effective diffusion coefficient of O\textsubscript{2} in the ash layer.
If Step (iii) controls the process:\(^4\)

\[
t = \frac{\rho_p}{b k_v C_{O_2, g}} (R - r_c)
\]

(S5)

\[
\tau = \frac{\rho_p}{b k_v C_{O_2, g}} R
\]

(S6)

where \(k_v\) is the first-order rate constant of Cu oxidation.

\(k_v\) in Equations (S1-S2) can be obtained as follows:\(^7\)

\[
k_v = \frac{1-\phi}{\phi} \left( \frac{D_{AB}}{d_p} \right) \text{Sh}
\]

(S7)

\[
\text{Sh} = Re^{1/2} Sc^{1/3}
\]

(S8)

\[
Re = \frac{ud_p}{(1-\phi)v}
\]

(S9)

\[
U = \frac{u_0}{A_c}
\]

(S10)

\[
Sc = \frac{v}{D_{AB}}
\]

(S11)

\[
D_{AB} = 10^{-3} T^{1.75} \left( \frac{1}{M_{O_2}} \frac{1}{M_{N_2}} \right)^{1/2} \frac{1}{p \left[ \frac{1}{(V_{O_2})^3 + (V_{N_2})^3} \right]^{2}}
\]

(S12)

All dimensionless numbers, Sh, Re, Sc, and symbols are defined in Table S2-S3. The diffusivity of O\(_2\) gas through the oxide ash layer (\(D_c\)) is first assumed to be 10\(^{-17}\) m\(^2\)/s at 300 °C based on the reported O\(_2\) gas diffusion coefficient in Cu\(_2\)O.\(^8\) After that, the actual \(D_c\) in our situation will be approximated by fitting to our experimental data.

For Equation (S3-S4), as the products of Cu oxidation are Cu\(_2\)O and CuO, the rate constants representing the processes of converting Cu to Cu\(_2\)O \((k_{v,1})\) and Cu\(_2\)O to CuO \((k_{v,2})\) are described as:\(^5\)

\[
k_{v,1} = 8.2 \times 10^6 \exp \left( \frac{-44\pm 15}{R T} \frac{kJ}{mol} \right) (s^{-1})
\]

(S13)
\[ k_{v,2} = 1.0 \times 10^7 \exp \left( \frac{-55 \pm 15 \text{kJ/mol}}{RT} \right) \text{ (s}^{-1} \text{)} \] (S14)

The carrier gas was assumed to be pure N\textsubscript{2} gas when calculating the kinematic viscosity (\( \nu \)), which is 4.8\times 10^{-5} \text{ m}^2/\text{s} based on the dynamic viscosity of N\textsubscript{2} gas at 300 °C and 1.01\times 10^5 \text{ Pa}.^9

For Cu particles, the oxidation products include CuO and Cu\textsubscript{2}O (Fig. 8, main text). As shown in Table S1, Step (ii), internal diffusion of O\textsubscript{2} gas through porous oxide ash layer controls the process in both scenarios.

For CuSn\textsubscript{0.05} particles, the oxidation products are Cu\textsubscript{2}O and SnO\textsubscript{2} (Fig. 8, main text). Step (ii) is the rate-limiting step. Detailed results are shown in Table S1.

For CuSn\textsubscript{0.1} particles, the oxidation products are Cu\textsubscript{2}O and SnO\textsubscript{2} (Fig. 8, main text). Step (ii) controls the process. Detailed results are shown in Table S1.

Therefore, the oxidation of Cu, CuSn\textsubscript{0.05}, and CuSn\textsubscript{0.1} particles are all controlled by internal diffusion of O\textsubscript{2} gas through the oxide ash layer based on SCM simulation.

b) Detailed procedures to obtain the \( D_e \)

In the SCM simulation, we utilized a diffusion coefficient of O\textsubscript{2} gas through Cu\textsubscript{2}O layer at 300 °C obtained from the literature, 10\textsuperscript{17} \text{ m}^2/\text{s} at 300 °C,\textsuperscript{8} which may not represent the internal diffusion of O\textsubscript{2} in our system. Thus, the actual diffusion coefficients in Equations (S3-S4) were fitted. To simplify the fitting model,

\[ x = [1 - 3\left( \frac{r_c}{R} \right)^2 + 2\left( \frac{r_c}{R} \right)^3] \] (S15)

Then Equation (S3) becomes:

\[ t = \frac{\rho_p R^2}{6b D_e CO_{2,b}} x \] (S16)
To obtain the actual $D_e$, the results in Fig. 7 (main text) need to be converted from $(\Delta m/m$ vs. $t)$ to ($t$ vs. $x$). The $r_c/R$ in Equation (S3) can be obtained by assuming the thickness of the oxide layer was uniform on the particle surface. Therefore, the volume of oxide layer can be calculated as:

$$V = \frac{4}{3} \pi (R^3 - r_c^3) \quad (S17)$$

The relative weight gain caused by oxidation is:

$$\frac{\Delta m}{m} = \frac{V_{\rho_p} \frac{2 M_w O}{M_w} \frac{2}{b}}{V_{\rho_p}} \quad (S18)$$

**Cu particles:**

To convert the results in Fig. 7 of main text ($\Delta m/m$ vs. $t$) into $t$ vs. $x$, equations are also derived based on the two situations when Cu$_2$O and CuO were the oxidation products.

If Cu is oxidized to Cu$_2$O, $b=4$. Then Equation (S18) can be converted into:

$$\frac{\Delta m}{m} = \frac{4 \frac{\pi (R^3 - r_c^3) \rho_{Cu}}{M_w}}{\frac{2}{M_w} \frac{2}{b} \frac{2}{\pi R^3 \rho_{Cu}} \frac{2}{M_w} \frac{2}{b}} = \frac{M_{wO}}{2 M_w \rho_{Cu}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad (S19)$$

When Cu is assumed to be directly oxidized into CuO, $b=2$. Then:

$$\frac{\Delta m}{m} = \frac{4 \frac{\pi (R^3 - r_c^3) \rho_{Cu}}{M_w}}{\frac{2}{M_w} \frac{2}{b} \frac{2}{\pi R^3 \rho_{Cu}} \frac{2}{M_w} \frac{2}{b}} = \frac{M_{wO}}{M_w \rho_{Cu}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad (S20)$$

The curves representing the $t$ vs. $x$ are presented in Fig. S13a-b. In the case of Cu$_2$O as the main product, the results in Fig. S13a are not well explained by SCM. In the SCM, Equation (S16) is linear and its slope is a monotonic function of $D_e$. If the oxidation product is CuO, the curve is still not linear (Fig. S13b). However, $D_e$ is $2.2 \times 10^{-13}$ m$^2$/s, if we fit the non-linear curve to a linear equation.

**CuSn$_{0.05}$ particles:**
Equation (S18) can be transformed into the following equation, because the oxidation products are Cu$_2$O and SnO$_2$ (Fig. 8, main text):

\[
\frac{\Delta m}{m} = \frac{\frac{4}{3}\pi(R^3-r_c^3)\rho_{\text{CuSn}0.05}}{\frac{M_{\text{CuSn}0.05}}{2}} \rho_{\text{CuSn}0.05} = \frac{0.6M_{\text{O}}}{M_{\text{CuSn}0.05}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad (S21)
\]

By applying Equation (S16) and (S21), curves in Fig. 7 ($\Delta m/m$ vs. $t$) can be converted into $t$ vs. $x$. The result is shown in Fig. S13c.

**For CuSn$_{0.1}$ particles:**

Equation (S18) can be transformed into following equation, because the oxidation products are Cu$_2$O and SnO$_2$ (Fig. 8, main text):

\[
\frac{\Delta m}{m} = \frac{\frac{4}{3}\pi(R^3-r_c^3)\rho_{\text{CuSn}0.1}}{\frac{M_{\text{CuSn}0.1}}{2}} \rho_{\text{CuSn}0.1} = \frac{0.7M_{\text{O}}}{M_{\text{CuSn}0.1}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad (S22)
\]

By applying Equations (S16) and (S22), curves in Fig. 7 ($\Delta m/m$ vs. $t$) can be converted into $t$ vs. $x$. The result is illustrated in Fig. S13d.
**Table S1.** Simulation results of particle oxidation at 300 °C in a packed-bed reactor by shrinking-core model. The diffusion coefficients listed here are obtained by fitting the experimental results, as shown in Fig. S13. The reported diffusion coefficients are $10^{-17}$ m²/s for both situations of O$_2$ through Cu$_2$O and O$_2$ through SnO$_2$ and at 300 °C.$^8,^{10}$

<table>
<thead>
<tr>
<th>Rate-limiting step</th>
<th>Particles</th>
<th>Cu</th>
<th>CuSn$_{0.05}$</th>
<th>CuSn$_{0.1}$</th>
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</thead>
<tbody>
<tr>
<td>$\rho_0$</td>
<td>1.4×10$^5$ mol/m³</td>
<td>1.4×10$^5$ mol/m³</td>
<td>1.3×10$^5$ mol/m³</td>
<td></td>
</tr>
<tr>
<td>$M_w$</td>
<td>64 g/mol</td>
<td>66 g/mol</td>
<td>69 g/mol</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>CuSn$_{0.05}$</th>
<th>CuSn$_{0.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sc$</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>$Re$</td>
<td>2.1×10$^5$</td>
<td>2.1×10$^5$</td>
<td>2.1×10$^5$</td>
</tr>
<tr>
<td>$Sh$</td>
<td>8.1×10$^3$</td>
<td>8.1×10$^3$</td>
<td>8.1×10$^3$</td>
</tr>
<tr>
<td>$k_g$</td>
<td>1.1 m/s</td>
<td>1.1 m/s</td>
<td>1.1 m/s</td>
</tr>
<tr>
<td>$\tau$</td>
<td>0.013 s, Cu$_2$O</td>
<td>0.013 s, Cu$_2$O</td>
<td>0.013 s</td>
</tr>
</tbody>
</table>

**External diffusion of O$_2$ gas to particle surface**

<table>
<thead>
<tr>
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<th>Cu</th>
<th>CuSn$_{0.05}$</th>
<th>CuSn$_{0.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$</td>
<td>2.2×10$^{-13}$ m²/s</td>
<td>8.2×10$^{-14}$ m²/s ($r_d/R \geq 0.9$)</td>
<td>3.5×10$^{-14}$ m²/s ($r_d/R \leq 0.9$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>4.2×10$^6$ min, Cu$_2$O</td>
<td>4.2×10$^6$ min</td>
<td>4.3×10$^6$ min</td>
</tr>
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</table>

**Internal diffusion of O$_2$ gas through oxide ash**

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>CuSn$_{0.05}$</th>
<th>CuSn$_{0.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_v$</td>
<td>800 s$^{-1}$ Cu$_2$O</td>
<td>800 s$^{-1}$ Cu$_2$O</td>
<td>800 s$^{-1}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>5.3×10$^{-5}$ s Cu$_2$O</td>
<td>5.4×10$^{-5}$ s Cu$_2$O</td>
<td>5.4×10$^{-5}$ s</td>
</tr>
</tbody>
</table>

**Chemical reaction of O$_2$ with metal core**
Fig. S13 Oxidation time ($t$) vs $x$ of Cu particles with the assumption that the product of Cu oxidation is Cu$_2$O (a) and CuO (b) at 300 °C. (c)-(d) Plots of oxidation time ($t$) vs $x$ of CuSn$_{0.05}$ (c) and CuSn$_{0.1}$ (d) particles. $x$ is a variable defined by Equation (S15). The internal diffusivity of O$_2$ through oxide ash layer ($D_e$) is obtained by fitting the curves in (a-d) by Equation (S16). The oxidation is conducted in O$_2$-He flow with 1.4 vol % O$_2$. The diffusion coefficients obtained are $10^3$ – $10^4$ higher than reported values for the diffusion coefficients, which are $10^{-17}$ m$^2$/s for both situations of O$_2$ through Cu$_2$O and O$_2$ through SnO$_2$ and at 300 °C.$^8,10$
Table S2. Variables used in modeling with their definitions and values

<table>
<thead>
<tr>
<th>Variables</th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
</table>
| $\rho_{Cu}$ | Density of Cu | $8.9 \times 10^3$ kg/m$^3$
| | | $1.4 \times 10^5$ mol/m$^3$ [$^6$] |
| $\rho_{Sn}$ | Density of Cu | $7.3 \times 10^3$ kg/m$^3$
| | | $6.1 \times 10^4$ mol/m$^3$ [$^6$] |
| $\rho_{Cu2O}$ | Density of Cu$_2$O | $6.0 \times 10^3$ kg/m$^3$
| | | $4.2 \times 10^4$ mol/m$^3$ [$^6$] |
| $R$ | Mean radius of particles | 355 nm [$^{11}$] |
| $d_p$ | Mean diameter of particles | 710 nm [$^{11}$] |
| $\Phi$ | Porosity | 0.4 [$^5$] |
| $U$ | Superficial velocity | $6.5 \times 10^{-3}$ m/s |
| $u_0$ | inlet gas flow rate | 50 ml/min |
| $v$ | kinematic viscosity | $3.6 \times 10^{-4}$ m$^2$/s at 300 °C
| | | $6.1 \times 10^{-4}$ m$^2$/s at 500 °C [$^9$] |
| $D_{AB}$ | Gas-phase diffusivity | 0.65 cm$^2$/s at 300 °C
| | | 1.1 cm$^2$/s at 300 °C |
| $A_c$ | Cross-sectional area of pipe | $1.3 \times 10^{-4}$ m$^2$ |
| $M_{O2}$ | Molecular weight of O$_2$ | 32 g/mol |
| $M_{N2}$ | Molecular weight of N$_2$ | 28 g/mol |
| $P$ | Pressure | 1 atm |
| $V_{O2}$ | Diffusion volume for O$_2$ | 16.6 [$^{12}$] |
| $V_{N2}$ | Diffusion volume for N$_2$ | 17.9 [$^{12}$] |
Table S3. Parameters used in modeling with definitions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>Oxidation time</td>
<td>s or min</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Time for complete oxidation</td>
<td>s</td>
</tr>
<tr>
<td>( b )</td>
<td>Stoichiometry of particle oxidation</td>
<td>dimensionless</td>
</tr>
<tr>
<td>( k_g )</td>
<td>Mass transfer coefficient between fluid and particle</td>
<td>m/s</td>
</tr>
<tr>
<td>( C_{O_2,g} )</td>
<td>( O_2 ) gas concentration in the main stream</td>
<td>mol/m^3</td>
</tr>
<tr>
<td>( r_c )</td>
<td>Radius of metal core</td>
<td>nm</td>
</tr>
<tr>
<td>( D_e )</td>
<td>Effective diffusion coefficient of ( O_2 ) in the ash layer</td>
<td>m^2/s</td>
</tr>
<tr>
<td>( k_o )</td>
<td>The first-order rate constant</td>
<td>s^{-1}</td>
</tr>
<tr>
<td>( Sh )</td>
<td>Sherwood number</td>
<td>dimensionless</td>
</tr>
<tr>
<td>( Re )</td>
<td>Reynolds number</td>
<td>dimensionless</td>
</tr>
<tr>
<td>( Sc )</td>
<td>Schmidt number</td>
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</tr>
<tr>
<td>( k_{app} )</td>
<td>First order apparent rate coefficient</td>
<td>min^{-1}</td>
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</table>
4. References for Electronic Supplementary Information