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Ice-Crystallization Kinetics in the Catalyst Layer of a Proton-Exchange-Membrane Fuel Cell

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Nucleation and growth of ice in the catalyst layer of a proton-exchange-membrane fuel cell (PEMFC) are investigated using isothermal differential scanning calorimetry and isothermal galvanostatic cold-starts. Isothermal ice-crystallization rates and ice-nucleation rates are obtained from heat-flow and induction-time measurements at temperatures below 240 and 273 K for four commercial carbon-support materials with varying ionomer fraction and platinum loading. Measured induction times follow expected trends from classical nucleation theory and reveal that the carbon-support material and ionomer fraction strongly impact the onset of ice crystallization. Conversely, dispersed platinum particles play little role in ice crystallization. Following our previous approach, a nonlinear ice-crystallization rate expression is obtained from Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory. A validated rate expression is now available for predicting ice crystallization within water-saturated catalyst layers. Using a simplified PEMFC isothermal cold-start continuum model, we compare cell-failure time predicted using the newly obtained rate expression to that predicted using a traditional thermodynamic-based approach. From this comparison, we identify conditions under which including ice-crystallization kinetics is critical and elucidate the impact of freezing kinetics on low-temperature PEMFC operation. The numerical model illustrates that cell-failure time increases with increasing temperature due to a longer required time for ice nucleation. Hence, ice-crystallization kinetics is critical when induction times are long (i.e., in the “nucleation-limited” regime for \( T > 263 \) K). Cell-failure times predicted using ice-freezing kinetics are in good agreement with the isothermal cold-starts, which also exhibit long and distributed cell-failure times for \( T > 263 \) K. These findings demonstrate a significant departure from cell-failure times predicted using the thermodynamic-based approach.

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Following the same procedure, catalyst inks were prepared for three other carbon supports (containing no Pt): Black Pears BP120, BP460, and BP800 (Cabot Corporation, Boston, MA). Additionally, catalyst inks were made for Vulcan XC72 without Pt and with varying Carbon:Nafion mass ratios (5:1, 5:4, and 5:8) for BP800 and Vulcan XC72. Unless otherwise stated, the Carbon:Nafion mass ratio is 5:2.

In all cases, catalyst inks (approximately 6 μL) were pipetted directly into 20-μL aluminum DSC pans (PerkinElmer Inc., Waltham, MA) and dried at 298 K under vacuum (4.7 kPa) to avoid cracking caused by rapid solvent evaporation. Dried samples were then saturated with Ultrapure Milli-Q (Millipore, Billerica, MA) distilled/deminized water in a home-built vacuum chamber for 1 h at 4.7 kPa. Following evaporation, excess surface water was removed by lightly blotting with Fisherbrand weighing paper (Fisher Scientific, Pittsburgh, PA). Water content was determined gravimetrically; measured values were consistent with integrated peak areas generated from DSC. Water loss by evaporation during DSC experiments was negligible. All catalyst water saturations are calculated from measured water contents to be between 78% and 94%, corresponding to typical porosities of 0.5 and 0.6, respectively.5,18,19,23

**Differential scanning calorimetry.**—A PerkinElmer 6000 DSC (PerkinElmer Inc., Waltham, MA) with a liquid-nitrogen chiller measured heat-flow rate from the sample over time. The DSC was calibrated as described previously.20 Nitrogen served as the purge gas at a flow rate of 20 mL/min. Isothermal crystallization was carried out from 240 to 273 K. Water-saturated catalyst samples were placed into the DSC at 300 K and cooled to the desired temperature at 105 K/min. A rapid cooling rate was chosen to reach the isothermal freezing temperature well before the onset of crystallization. Samples were then held at the subcooled temperature until crystallization was complete. Experiments were performed at various subcoolings, ΔT = To − T, defined as the magnitude of the difference in the temperature of freezing and 273 K.

**Isothermal cold-start.**—Membrane electrode assemblies (MEAs) were provided by Ion Power (Ion Power, Inc., New Castle, DE). MEAs consisted of a DuPont Nafion XL membrane, a TEC10EA40 cathode, and a TEC10V20E anode with 0.15 and 0.07 mg/cm2 Pt loading, respectively. Ion Power purchased the cathode and anode catalysts from Tanaka Kikinzoku Kogyo K.K. (Tanaka Kikinzoku, Tokyo, Japan) and mixed them with a Nafion solution to form an ink that was then painted on a web prior to transfer to the membrane. MEAs were assembled in single 50-cm2 quad-serpentine fuel-cell hardware with cooling loops machined into both end plates. Cells were tested on a Fuel Cell Technologies testing stand (Fuel Cell Technologies, Inc., Albuquerque, NM) and cooled using a Neslab ULT-80 bath circulator.

Prior to each isothermal cold-start experiment, cells were conditioned at a current density of 1000 mA/cm2 at 353 K and 100% relative humidity. Following, cathode and anode flow channels were purged with 1000 mL/min of nitrogen gas for 30 s to prevent water from forming ice and clogging the flow fields. Cells were then cooled to the desired isothermal freezing temperature and equilibrated at that temperature for 30 min. Isothermal cold-start experiments were carried out with 500 sccm of dry hydrogen and air. Following an initial current ramp of 0.4 mA/cm2/s, current of 20 mA/cm2 was applied until the cell voltage decayed to 0 mV. The cells were then heated to 353 K for characterization, and cycling was repeated.

**Experimental Results**

**Ice-crystallization kinetics.**—Figure 1 shows a typical exotherm of heat flow and sample temperature versus time for a water-saturated Vulcan XC72 catalyst. The sample was cooled at 105 K/min to 257 K (i.e., ΔT = 16 K), where isothermal crystallization commenced (point A in Figure 1). Heat flow due to liberation of the enthalpy of crystallization from point A is evident until a minimum is observed at point B, after which crystallization slows significantly until complete crystallization at point C. To obtain the gas-free ice volume fraction within the catalyst pores as a function of time, φ(t), crystallization exotherms were integrated from point A to point C, according to

\[
\phi(t) = \frac{1}{\int_0^\infty Q(t) dt} \int_0^t Q(t) dt
\]

where \(Q(t)\) is heat-flow rate from the DSC. Crystallization is preceded by an induction time, \(\tau_i\), defined as the time elapsed between the sample temperature becoming isothermal and the onset of the crystallization peak (point A), about 225 s in Figure 1.

Figure 2 displays number-average induction time, \(\bar{\tau}_i\), as a function of subcooling, ΔT, for five water-saturated catalysts: 20 wt% Pt on Vulcan XC72 (triangles), Vulcan XC72 without Pt (squares), BP120 (inverted triangles), BP460 (diamonds), and BP800 (circles). Symbols denote average-\(\tau_i\) measurements for a minimum of 25 experiments.
Typical error bars for BP120 are discussed below. Solid lines are drawn according to classical nucleation theory (CNT), as discussed later. Several features are salient. In all cases, \( \bar{\tau}_i \) decreases with increasing \( \Delta T \), as expected. For Vulcan XC72, measurements for Vulcan XC72 are similar to those for BP120 and BP460/800, but are shifted to larger \( \Delta T \) by about 3 and 8 K, compared to those for BP120 and BP460/800, respectively. This result indicates that the specific carbon-support material impacts the onset of ice crystallization. Similar \( \bar{\tau}_i \) measurements for Vulcan XC72 with and without added platinum (compare triangles and squares) at nearly all \( \Delta T \) reveals that dispersed platinum particles, with diameters ranging from 3–5 nm, play little role in ice crystallization at typical loadings.

Example error bars in Figure 2 indicate the maximum range of observed \( \tau_i \). For all catalysts, \( \tau_i \) was measured repeatedly to investigate the statistical nature of ice crystallization and to obtain pseudo-steady-state ice-nucleation rates, as discussed below. Representative results for BP120 are shown in Figure 3. Figure 3 displays at least 25 induction-time measurements at a subcooling of (a) 14.75 K and (b) 20 K for BP120. Horizontal dashed lines indicate the number-average induction time, \( \bar{\tau}_i \).

Figure 4 shows ice-crystallization kinetics, \( \phi(t) \) versus \( t \), calculated from Eq. 2 for the five water-saturated catalysts in Figure 2 (for specific samples with \( \tau_i \approx \bar{\tau}_i \)). Symbols denote 20 wt% Pt on Vulcan XC72 (triangles), Vulcan XC72 without Pt (squares), BP120 (inverted triangles), BP460 (diamonds), and BP800 (circles). Filled symbols correspond to a subcooling of 17.5 K, whereas open symbols (circles) correspond to a subcooling of 11 K. Solid and dashed lines are predictions of \( \phi(t) \) using Eqs. 3 and 4, at subcoolings of 17.5 and 11 K, respectively.

Vulcan XC72 (triangles), Vulcan XC72 without Pt (squares), BP120 (inverted triangles), BP460 (diamonds), and BP800 (circles). Filled symbols correspond to a subcooling of 17.5 K, whereas open symbols (circles) correspond to a subcooling of 11 K. Solid and dashed lines are predictions of \( \phi(t) \) from Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory at \( \Delta T = 17.5 \) K and 11 K, respectively, as discussed below. At each subcooling, \( \tau_i \) was subtracted from the total time so that all curves are compared on a single time scale. Complete ice-crystallization times (taken when \( \phi(t) = 0.99 \)) are 13.3, 13.7, 22.0, and 24.1 s for BP460, BP800, BP120, and Vulcan XC72 at 17.5 K, respectively. Similar to Figure 2, Figure 4 illustrates that the carbon-support material appreciably impacts ice-freezing kinetics. Likewise, nearly identical \( \phi(t) \) for Vulcan XC72 with and without platinum demonstrates that dispersed platinum does not significantly affect the kinetics of ice-crystallization. As \( \Delta T \) decreases from 17.5 K to 11 K for BP800, complete ice-crystallization times increase from 13.3 to 27.7 s. This result reiterates that subcooling, \( \Delta T \), is the driving force for ice crystallization.

Figure 5. Typical evolution of MEA cell voltage during isothermal galvanostatic cold-start from 267 K. Squares denote cell voltage, whereas circles represent current density. The symbol \( t_{\text{fail}} \) labels the cell-failure time.
Isothermal cold-start.---Figure 5 shows a typical evolution of MEA cell voltage (squares) during isothermal cold-start from a subcooling of 6 K at a current density (circles) of 20 mA/cm². Initially, cell voltage decreases from 1.0 to 0.8 V during the current ramp of 0.4 mA/cm²/s. Following a constant current density of 20 mA/cm², cell voltage remains constant until failure (i.e., when cell voltage rapidly decreases to 0 mV) as a result of ice formation within the cathode.1–19,35

We define the cell-failure time, \( t_{\text{fail}} \), as the time elapsed between the onset of constant cell voltage and 0 mV. We do not include the 30-min stabilization period when determining measured \( t_{\text{fail}} \). To demonstrate applicability of ice-freezing kinetics to PEMFC cold-start, isothermal \( t_{\text{fail}} \) was measured as a function of \( \Delta T \).

Figure 6 plots isothermal \( t_{\text{fail}} \) versus \( \Delta T \) at a current density of 20 mA/cm². Solid and dashed lines are discussed below in the model section and Appendix A. As \( \Delta T \) increases, \( t_{\text{fail}} \) decreases substantially due to a shorter time required for ice nucleation (i.e., decreased \( \tau_i(\Delta T) \) in Figure 2). For example, \( t_{\text{fail}} \) decreases from 15.5 and 33 h to 0.19 and 0.2 h for an increase in \( \Delta T \) from 5 to 10 K, respectively. The variance (not shown) between repeated \( t_{\text{fail}} \) measurements also decreases significantly with increasing \( \Delta T \), suggesting that stochastic nucleation events are critical at low subcoolings. This finding is consistent with narrowing \( \tau_i \)-distributions for increased \( \Delta T \) (compare Figure 2a and Figure 2b). Since a single induction time corresponds to a given cell-failure time, \( t_{\text{fail}} \) values are similarly distributed. Our measured isothermal cell-failure times are similar to those obtained by Oberholzer et al.,8 who observed a Poisson distribution of MEA-cell-failure times during isothermal galvanostatic cold-start from 258 to 268 K using neutron imaging.

Ice-Crystallization Rate Expression

To obtain a predictive ice-crystallization rate equation, \( \phi(t) \) and \( \bar{\tau}_i \) must be specified a priori. Following our previous development,20 we employ Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory and classical nucleation theory (CNT). We summarize the procedure below. Additional detail is available elsewhere.20

Within the JMAK framework,20,25-28 \( \phi(t) \) is determined by a convolution integral over nucleation and growth rates (see Eq. 4 of Dorsch et al.)20 For spherical, heat-transfer-limited growth under isothermal conditions in a closed system, the convolution integral reduces considerably. In this case, \( \phi(t; T) \) is given by\(^{20,21} \)

\[
\phi(t; T) = 1 - \exp\left[-k(T)[t - \bar{\tau}_i(T)]^{1/2}\right] \tag{3}
\]

with

\[
k(T) = \frac{64\pi}{15} g(\theta) J(n_0^3 T) \theta^{1/2}, \tag{4}
\]

where \( \alpha_L \) is liquid thermal diffusivity, \( J(T) \) is the pseudo-steady-state nucleation rate, \( n_0(\Delta T) \) is a dimensionless temperature-dependent growth parameter (see Eq. 9 of Dorsch et al.),\(^{20} \theta \) is the contact angle of the ice/water/substrate triple line, and \( g(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4 \) for heterogeneous nucleus growth on a flat surface. Eqs. 3 and 4 predict the ice-crystallization rates, \( \bar{\tau}_i(t; T; \theta) = \delta(\phi(t; T))/\partial t \),\(^{21} \) once the unknowns \( J(T), \theta, \) and \( \bar{\tau}_i \) are specified.

To obtain \( \bar{\tau}_i \), the definition suggested by Kaschiev\(^{20} \) is adopted

\[
\bar{\tau}_i(T) = \frac{1}{J(V_o)} + \tau_i(T), \tag{5}
\]

where \( V_o \) is liquid volume of a water-saturated cCL. The first term on the right of Eq. 5 is the expectation time for the appearance of a critical nucleus while the second term is the time required for critical nuclei to form and grow to a size detectable by the DSC. For spherical, heat-transfer-limited growth,\(^{24,25} \bar{\tau}_i(T) = (15\alpha_L/64\pi\theta g(\theta) J(n_0^3 T) \theta^{1/2})^{1/2}, \) where \( \alpha_L \) is an instrument-specific constant, is 0.0173 for our DSC.\(^{21} \) Thus, estimation of \( \bar{\tau}_i \) requires both \( J(T) \) and \( \theta \).

Following our previous work,\(^{20,21} \) \( J(T) \) is obtained from repeated \( \tau_i \) measurements at a minimum of five subcoolings (e.g., see Figure 3). To acquire \( J(T) \), a Poisson distribution is fit to measured \( \tau_i \) probability distributions obtained from the repeated \( \tau_i \) measurements.\(^{20,24} \) CNT specifies the temperature-dependence of \( J(T) \).

\[
J(T) = A \exp\left[\frac{-B}{T(\Delta T)^2}\right]. \tag{6}
\]

Eq. 6 indicates that a plot of \( \ln J \) versus \( T^{-1}(\Delta T)^{-2} \) produces a straight line with an intercept \( \ln A \) and slope \( -B \). Figure 7 confirms this behavior for the four PEMFC catalysts shown in Figure 2 (filled symbols). A Toray gas-diffusion layer (GDL) (open symbols) is included for comparison.\(^{20} \) In all cases, \( \ln J \) versus \( T^{-1}(\Delta T)^{-2} \) is linear with 0.91 < \( R^2 < 0.99 \), where \( R^2 \) is the square of the Pearson correlation coefficient. Obtained ice-nucleation-rate parameters, \( A \) and \( B \) in Equation 6, are provided in Table I, and their physical significance is discussed in Appendix B.

With \( J(T) \) specified, Eqs. 3–6 provide a predictive ice-crystallization rate valid within PEMFC cCLs. In all subsequent calculations, \( \alpha_L = 1.4 \times 10^{-7} \text{m}^2/\text{s} \) and \( \theta = 60^\circ \) for BP460/BP800 and XC72/BP120, respectively. Values of \( \theta \) are discussed in detail in Appendix B. With these independently determined parameters, lines
Table I. Ice-Nucleation Rate Parameters.

<table>
<thead>
<tr>
<th>cCL/GDL</th>
<th>A (\times 10^{-8}) nuclei m(^{-3}) s(^{-1})</th>
<th>B (\times 10^{-4}) K(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC72</td>
<td>112.7</td>
<td>40.3</td>
</tr>
<tr>
<td>BP800</td>
<td>287.0</td>
<td>44.1</td>
</tr>
<tr>
<td>BP460</td>
<td>9.0</td>
<td>12.8</td>
</tr>
<tr>
<td>BP800</td>
<td>6.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Toray GDL</td>
<td>7.9</td>
<td>9.4</td>
</tr>
</tbody>
</table>

\(^*\)From Dursch et al.\(^20\)

Table II. Model Parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>cCL</th>
<th>cGDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon_o)</td>
<td>0.6 [18]</td>
<td>0.8 [20]</td>
</tr>
<tr>
<td>(\rho C_P) (\text{kJ m}^{-3} \text{ K}^{-1})</td>
<td>990 [19]</td>
<td>970 [19]</td>
</tr>
<tr>
<td>(k_T) (\text{W m}^{-1} \text{ K}^{-1})</td>
<td>1.2 [18]</td>
<td>1.5 [18, 34]</td>
</tr>
<tr>
<td>(k_a) (\text{m}^2)</td>
<td>(1.6 \times 10^{-15}) [19]</td>
<td>(3.4 \times 10^{-12}) [19]</td>
</tr>
<tr>
<td>(\eta_0) (V)</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>(U_{eff}) (\text{U (W m}^{-2} \text{ K}^{-1})</td>
<td>-0.012 [19]</td>
<td>-</td>
</tr>
<tr>
<td>(A \times 10^{-8}) (nuclei m(^{-3}) s(^{-1}))</td>
<td>90 [18]</td>
<td>100 [18]</td>
</tr>
<tr>
<td>(B \times 10^{-4}) (K(^3))</td>
<td>12.8 to 40.3</td>
<td>9.4 [20]</td>
</tr>
</tbody>
</table>

\(^1\)calculated from measured cell voltage in Figure 5.

Isothermal PEMFC Cold-Start Model

Continuum model.— Eqs. 3–6 provide an ice-crystallization rate expression valid within PEMFC catalyst layers. To investigate the importance of ice-crystallization kinetics, we compare predicted \(\bar{t}(T)\) with the newly obtained rate expression relative to that predicted using a traditional thermodynamic-based approach (e.g., Eq. 1)\(^17\)–\(^19\) in a simplified isothermal PEMFC cold-start continuum-finite-difference model (see Appendix A).

Figure 8 illustrates the simplified 1-D geometry of the PEMFC. Dashed lines outline the spatial domain (i.e., we consider only the cCL and cGDL). Symbols a and c label the anode and cathode, respectively. We neglect water transport and subsequent freezing within the anode, since the diffusivity of water in a PEM is negligible at subfreezing temperatures.\(^5\) Meng,\(^14\) Mao et al.,\(^15,16\) Jiao et al.,\(^17\) and Balliet et al.,\(^18,19\) have identified that the temperature dependences of both \(\bar{t}(T)\) and \(\phi(T)\) are correctly captured. Importantly, lines in Figure 4 at \(\Delta T = 17.5\)K show that complete ice-crystallization times are shorter for BP800 and BP120 than those for Vulcan XC72 due to an increased ice-nucleation rate (i.e., larger \(A\) and/or smaller \(B\) in Table I) and consequently, a decreased \(\bar{t}\).

In the current study, the ice-crystallization rate depends on the kinetics of ice nucleation and growth rather than on ice/water phase equilibria. Following our previous work,\(^21\) the ice-generation rate under pseudo-isothermal conditions, \(R_i(T, \phi)\) (i.e.,\(^*\) generated ice volume)/(water plus ice volume)/time) is given by

\[
R_i(T, \phi) = k(T) \bar{t}(T)^{2/5} \left(1 - \phi \right)^{-3/5} \left[\ln(1 - \phi)\right]^{1/5} \quad \text{for } t \geq \bar{t},
\]

where \(T_c\) is number-average crystallization temperature, \(\bar{t}\) is number-average non-isothermal induction time, \(\phi\) is gas-free volume fraction of ice within the pores defined by \(\phi = S_l/(S_l + S_i)\), and \(k(T)\) is given by Eq. 4, but evaluated at the number-average crystallization temperature, \(T_{c}\).\(^21\) Eq. 7 applies only for \(t > \bar{t}\) (i.e., the non-isothermal induction time), \(\bar{t}\) is given by\(^21\)

\[
\bar{t} = \frac{\int_0^{\bar{t}} dt}{\bar{t}(T)} = 1.
\]

\(\bar{t}(T)\) follows from the first term on the right of Eq. 5, as well as Eq. 6. We note that for calculation of \(\bar{t}(T)\) during PEMFC cold-start, the instrument-specific growth term does not apply. In Eq. 5, \(\bar{t}(T)\) depends on liquid volume in either the cCL or GDL, \(V_{\text{eff}}\). To eliminate the volume-dependence of \(\bar{t}(T)\) in the continuum MEA cold-start model, we evaluate \(\bar{t}(T)\) for large \(V_{\text{eff}}\) (i.e., the fastest onset of ice crystallization). The approximation of “large volume” is valid since for small \(\Delta T\), \(\bar{t}(T)\) depends only on \(J(T)\) and not on \(V_{\text{eff}}\).\(^21\)

Coupled, nonlinear differential-algebraic equations (Eqs. 4–8 and A1–A6) are solved simultaneously subject to the boundary conditions provided in Figure 8. \(U_{eff}\) is the overall effective heat-transfer coefficient that includes heat conduction through the anode and external convection. In all cases, temperature is uniform at the isothermal ambient subcooling, \(\Delta T = 273.15 - T_0\), where \(T_0\) is the ambient temperature. Similar to Jiao et al.,\(^17\) and Balliet et al.,\(^18,19\) the initial liquid-water saturations, \(S_{\text{L}}\), are 0.34 and 0.22 in the cCL and cGDL, respectively. In both the cCL and cGDL, initial gas pressure is uniform at 101.3 kPa. Equations are solved numerically in Matlab R2010a (The Math Works Inc., Natick, MA) using finite differencing and Newton iteration to resolve nonlinearities with a tolerance of \(10^{-7}\), a time step of \(10^{-2}\) s, and 50 mesh elements. A Thomas-algorithm inversion scheme BAND\(4\) solves the resulting tridiagonal matrices.\(^21\) All model parameters are reported in Table II.

Model results.— Figure 9 displays typical calculated liquid-water saturations, \(S_{\text{L}}\), as a function of time, \(t\), at the coldest boundaries of the cCL \((x = L)\) and cGDL \((x = 0)\) at equal subcoolings, \(\Delta T\), of 10 K at \(x = 0, L\) and \(i = 20\) mA/cm\(^2\). Solid lines reflect the proposed ice-crystallization kinetic model (i.e., Eqs. 4–8) for the Vulcan XC72 catalyst and the Toray cGDL in Table I. Initially, \(S_{\text{L}}\) slightly increases in both the cCL and cGDL as a result of water generation in the cCL and subsequent migration to the cGDL due to a gradient in capillary pressure. \(S_{\text{L}}\) continues to increase until crystallization first commences.

Figure 8. Schematic and boundary conditions for the simplified 1-D PEMFC cold-start model. Dashed lines represent the modeling domain. Subscript \(x\) indicates partial differentiation. Prefix letters a and c denote the anode and cathode, respectively.
in the cCL at the number-average non-isothermal induction time, $\bar{\tau}_{\text{cCL}}$, where liquid water rapidly transforms into ice.\textsuperscript{20,23}\textsuperscript{,34} In the cCL, $\bar{\tau}_{\text{cCL}}$ is considerably longer than that in the cGDL due to slower ice nucleation rates (see Table 1). Consequently, $S_I$ increases over a longer time period prior to freezing. $S_I$ and $T$ profiles at given times are omitted, as both are essentially uniform due to a small Biot number ($Bi = 0.002$) and a fast time-scale for water movement.

Conversely, dashed and dotted lines in Figure 9 are calculated using a thermodynamic-based approach (i.e., Eq. 1).\textsuperscript{18} Dashed and dotted lines correspond to $k_f = 0.25$ and $1$ kg/m$^3$s, respectively.\textsuperscript{18} In this approach, freezing begins once the local liquid temperature is less than the equilibrium freezing temperature, $T_{\text{f}}$. For $\Delta T = 10$ K, $T$ is well below $T_{\text{f}}$ within the cCL ($270.2$ to $271.1$ K)\textsuperscript{11} and within the cGDL ($273.0$ K).\textsuperscript{11}\textsuperscript{,35} Accordingly, $S_I$ decreases abruptly in both cases due to nearly immediate freezing. In this calculation, we neglect the relatively narrow pore-size distributions of the cGDL or cCL.\textsuperscript{8,19} Figure 9 highlights the importance of $\bar{\tau}_I$ for forestalling freezing especially in the cCL.

The likelihood of successful cold-start depends strongly on temperature through $\bar{\tau}_I$. Thus, to elucidate those conditions for which including ice-crystallization kinetics is critical, we examine isothermal cell-failure time for various subcoolings, $\Delta T$. We define a cell-failure time, $\bar{\tau}_{\text{fail}}$, as the time when ice reaches a critical saturation, $S_{I\text{fail}}$, thereby chocking the cell.\textsuperscript{14} In all cases, $\bar{\tau}_{\text{fail}}$ is taken as 0.38 and 0.55 in the cCL and cGDL, respectively. In the cCL, $\bar{\tau}_{\text{fail}} = 0.38$ is obtained from a fit of measured cell voltage versus time at $\Delta T = 10$ K and $i = 20$ mA/cm$^2$. In the cGDL, however, $\bar{\tau}_{\text{fail}} = 0.55$ is taken as the saturation when the effective oxygen diffusion coefficient reaches a limiting value,\textsuperscript{36,37} taken as 0.03 in all cases. A partially ice-saturated cCL and cGDL (i.e., $S_{I\text{fail}} < 1$) at cell failure are consistent with experimental observation.\textsuperscript{34,38}

Solid and dashed lines in Figure 6 compared predicted to measured (symbols) $\bar{\tau}_{\text{fail}}$ versus $\Delta T$ for an isothermal galvanostatic cold-start. Solid lines correspond to ice-crystallization kinetics (i.e., Eqs. 4–8) for two cCL carbon-support materials with considerably different ice-crystallization kinetics: Vulcan XC72 and BP460. The dashed line is predicted using a traditional thermodynamic-based approach with $k_f = 0.25$ kg/m$^3$s.\textsuperscript{18} In all cases, $\bar{\tau}_{\text{fail}}$ decreases substantially with increasing $\Delta T$, in good agreement with experiment. In both the kinetic and thermodynamic approaches, $\bar{\tau}_{\text{fail}}$ decreases to a limiting value of approximately 0.1 h. Accordingly, two limiting regimes for $\bar{\tau}_{\text{fail}}$ are evident in Figure 6. For small subcoolings (i.e., $\Delta T < 3$ K and $\Delta T < 11$ K for thermodynamic and kinetic freezing, respectively), $\bar{\tau}_{\text{fail}}$ is limited by freezing, whereas for larger subcoolings, $\bar{\tau}_{\text{fail}}$ is limited by water production. Figure 9 illustrates the latter case. Here, predicted $\bar{\tau}_{\text{fail}}$ is larger than the time required for ice crystallization (i.e., 40 and 260 s in the cGDL and cCL, respectively), since $S_I < S_{I\text{fail}}$ upon complete crystallization of all liquid water present. $S_I$ increases further to $S_{I\text{fail}}$ only as newly-generated water freezes. In Figure 6, measured and predicted $\bar{\tau}_{\text{fail}}$ is for a current density, $i$, of 20 mA/cm$^2$. Significantly, our numerical model reveals that current densities greater than 20 mA/cm$^2$ likewise exhibit cell-failure times with two limiting regimes, as in Figure 6. Furthermore, $\bar{\tau}_{\text{fail}}$ decreases monotonically with increasing current density in the water-production-limited regime (i.e., $\Delta T > 11$ K), as discussed elsewhere.\textsuperscript{3,6–11,38}

In both the cCL and cGDL, $\bar{\tau}_I$ decreases significantly with increasing subcooling (e.g., see Figure 2). Consequently, as subcooling extends beyond $\Delta T = 11$ K, $\bar{\tau}_I$ is negligible in both cell domains, and ice-crystallization kinetics is well approximated by the thermodynamic-based approach. We conclude that including ice-crystallization kinetics is critical in the “nucleation-limited” regime (see Figure 14 of Dursch et al.\textsuperscript{10} where induction times are long (i.e., from $3 \leq \Delta T \lesssim 10$ K in Figure 6). However, the particular $\Delta T$ that establishes the “nucleation-limited” regime relies heavily on all heat transfer and kinetic parameters (e.g., $U$, $U_{\text{eff}}$, $k_f$, and $J(T)$). These controlling parameters can be adjusted to lengthen $\bar{\tau}_I$, significantly delaying or even preventing ice formation.\textsuperscript{34}

The ice distribution at cell failure in both the cCL and cGDL depends strongly on subcooling (i.e., Eq. 1).\textsuperscript{18} Figure 9 displays the ratio of spatially-averaged ice saturation in the cGDL to that in the cCL, $S_{I\text{GDL}}/S_{I\text{CCL}}$ (cGDL, as a function of subcooling, $\Delta T$, at a current density of 20 mA/cm$^2$. Solid lines are calculated using ice-crystallization kinetics in the BP460 and Vulcan XC72 cCLs, and the Toray cGDL. The dashed line is calculated using a typical thermodynamic-based rate expression (i.e., Eq. 1).\textsuperscript{18}
for ice propagation between the cCL and cGDL since the shortest induction time controls cell failure. Accordingly, the two limiting regimes in Figure 10 emphasize the importance of ice-crystallization induction time controls cell failure. Accordingly, the two limiting crystallization kinetics is critical when induction times are long using a traditional thermodynamic-based approach. Cell-failure times using the newly obtained rate expression to those predicted using the galvanostatic cold-start model, we compare cell-failure times predicted for four commercial carbon-support materials, with varying ionomer fraction and platinum loading. Measured isothermal ice-crystallization rates and ice-nucleation rates are obtained as a function of subcooling for four commercial carbon-support materials, with varying ionomer fraction and platinum loading. Significantly, cell-failure times predicted using the rate expression is obtained from Johnson-Mehl-Avrami-Kolmogorov theory.

To validate ice-crystallization kinetics within PEMFCs, we measure cell-failure time as a function of subcooling during isothermal galvanostatic cold-start in a commercial MEA. Significantly, cell-failure time decreases with decreasing temperature due to a shorter required time for ice nucleation. Using a 1D PEMFC isothermal numerical cold-start model, we compare cell-failure times predicted using the newly obtained rate expression to those predicted using a traditional thermodynamic-based approach. Cell-failure times predicted using ice-freezing kinetics are in good agreement with experiments. The PEMFC cold-start model demonstrates that ice-crystallization kinetics is critical when induction times are long (i.e., in the “nucleation-limited” regime for T > 263 K). However, the particular temperature that establishes the “nucleation-limited” regime relies heavily on all heat transfer and kinetic parameters. Accordingly, these controlling parameters can be adjusted to lengthen induction times, significantly delaying or even preventing ice formation.

Acknowledgments

This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, of the U. S. Department of Energy under contract number DE-AC02-05CH11231.

List of Symbols

\[ \begin{aligned}
A & \quad \text{ice-nucleation-rate constant (nuclei/m}^2\text{s)} \\
B & \quad \text{ice-nucleation-rate constant (K}^2\text{)} \\
\bar{C}_p & \quad \text{specific heat capacity (J/g-K)} \\
\Delta G^* & \quad \text{Gibbs-free energy of critical-nucleus formation (J)} \\
\Delta \tilde{H}_f & \quad \text{heat of fusion per mass of solid (kJ/kg)} \\
i & \quad \text{current density (A/m}^2\text{)} \\
J & \quad \text{pseudo-steady-state nucleation rate (nuclei/m}^2\text{s)} \\
k & \quad \text{overall crystallization rate constant (s}^{-2}\text{.5)} \\
k_0 & \quad \text{equilibrium freezing rate constant (kg/m}^2\text{s)} \\
k_b & \quad \text{Boltzmann constant (J/molecule/K)} \\
k_T & \quad \text{constant volume-averaged thermal conductivity (W/mK)} \\
P_C & \quad \text{capillary pressure, P}_C - P_L (\text{Pa}) \\
\dot{Q} & \quad \text{heat-flow rate (mW)} \\
* & \quad \text{critical-nucleus radius (nm)} \\
\dot{R}_1 & \quad \text{ice-generation rate ((generated ice volume)/(water plus ice volume)/time)} \\
\dot{R}_S & \quad \text{seed-particle radius (nm)} \\
S & \quad \text{saturation} \\
t & \quad \text{time (s)} \\
\tau \text{fail} & \quad \text{MEA-cell-failure time (s)} \\
\bar{T} & \quad \text{temperature (K)} \\
T_C & \quad \text{crystallization temperature (K)} \\
\Delta T & \quad \text{subcooling (K)} \\
U & \quad \text{overall heat transfer coefficient (W/m}^2\text{K)} \\
U_{eq} & \quad \text{effective overall heat transfer coefficient (W/m}^2\text{K)} \\
V & \quad \text{volume (m}^3\text{)} \\
x & \quad \text{denotes partial differentiation} \\
\alpha & \quad \text{thermal diffusivity (m}^2\text{s)} \\
\varepsilon & \quad \text{volume fraction} \\
\varepsilon_o & \quad \text{bulk porosity} \\
\gamma & \quad \text{surface tension (dyne/cm)} \\
\eta & \quad \text{viscosity (Pa-s)} \\
\eta_o & \quad \text{dimensionless thermal-growth constant} \\
\eta_s & \quad \text{surface overpotential (V)} \\
\theta & \quad \text{contact angle} \\
\Pi & \quad \text{Peltier coefficient (V)} \\
\rho & \quad \text{mass density (kg/m}^3\text{)} \\
\tau_g & \quad \text{time for nuclei grow to an instrument-detectable size (s)} \\
\tau_i & \quad \text{isothermal induction time (s)} \\
\tau_T & \quad \text{non-isothermal induction time (s)} \\
\phi & \quad \text{gas-free ice volume fraction} \\
\omega & \quad \text{instrument constant, 0.0173} \\
\Psi & \quad \text{heterogeneous nucleation shape factor in Eq. B1} \\
\text{Subscripts} & \\
a & \quad \text{anode} \\
c & \quad \text{cathode} \\
G & \quad \text{gas} \\
I & \quad \text{ice} \\
k & \quad \text{phase} \\
L & \quad \text{liquid water} \\
o & \quad \text{initial} \\
\text{Greek Letters} & \\
\alpha & \quad \text{thermal diffusivity (m}^2\text{s)} \\
\varepsilon & \quad \text{volume fraction} \\
\varepsilon_o & \quad \text{bulk porosity} \\
\gamma & \quad \text{surface tension (dyne/cm)} \\
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\theta & \quad \text{contact angle} \\
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\tau_g & \quad \text{time for nuclei grow to an instrument-detectable size (s)} \\
\tau_i & \quad \text{isothermal induction time (s)} \\
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\phi & \quad \text{gas-free ice volume fraction} \\
\omega & \quad \text{instrument constant, 0.0173} \\
\Psi & \quad \text{heterogeneous nucleation shape factor in Eq. B1} \\
\text{ Appendix A. PEMFC Cold-Start Continuum Model} \\

Within the cCL and cGDL, we write continuum differential equations and mass conservation balances for gas (G), liquid (L), and ice (I). In each subdomain, phase saturations sum to unity, i.e., \( S_G + S_L + S_I = 1 \), where the saturation of a phase \( S_k \), is defined as volume of phase \( k \) per pore volume, or \( \varepsilon \Phi_k / \varepsilon \), where \( \varepsilon \Phi_k \) is porosity of phase \( k \) and \( \varepsilon_o \) is bulk porosity. Upon thermal equilibrium among all phases, \( \varepsilon_i^\text{CL} = \varepsilon_i^\text{GDL} \), so that higher ice and water saturations choke the electrochemical production of liquid water. More involved models are discussed elsewhere.15–20

In each subdomain, gas-, liquid-, and ice-phase saturations obey the following mass conservation equation combined with Darcy’s law15–19

\[
\varepsilon_i \frac{\partial S_i}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\rho C_p \dot{Q}}{\eta_s} \frac{\partial \bar{P}_C}{\partial x} \right), \quad [A2]
\]

and

\[
\varepsilon_i \frac{\partial S_i}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\rho C_p \dot{Q}}{\eta_s} \frac{\partial \bar{P}_C}{\partial x} \right) - \rho v_s (S_L + S_I) R_I + R_{\text{cond}}. \quad [A3]
\]

Within the cCL and cGDL, we write continuum differential equations and mass conservation balances for gas (G), liquid (L), and ice (I). In each subdomain, phase saturations sum to unity, i.e., \( S_G + S_L + S_I = 1 \), where the saturation of a phase \( S_k \), is defined as volume of phase \( k \) per pore volume, or \( \varepsilon \Phi_k / \varepsilon \), where \( \varepsilon \Phi_k \) is porosity of phase \( k \) and \( \varepsilon_o \) is bulk porosity. Upon thermal equilibrium among all phases, \( \varepsilon_i^\text{CL} = \varepsilon_i^\text{GDL} \), so that higher ice and water saturations choke the electrochemical production of liquid water.15–20 More involved models are discussed elsewhere.15–20

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\]

and

\[
\varepsilon_i \frac{\partial S_i}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\rho C_p \dot{Q}}{\eta_s} \frac{\partial \bar{P}_C}{\partial x} \right) - \rho v_s (S_L + S_I) R_I + R_{\text{cond}}. \quad [A3]
\]
where $R_g = k_B T / F$ in the cCL and $R_{g,c}$ equals zero in the cGDL, $\eta$ is viscosity, $P$ is pressure, $M_{H_2O}$ is the molar mass of water, and $k_B T$ is the effective permeability of phase $k$ as a function of $T$. The first, second, and third terms on the right of Eq. A3 represent water movement due to a gradient in capillary pressure, $P_c = P_1 - P_2$, water depletion due to freezing, and water generation due to reaction, respectively. The effective permeabilities in Eqs. A2 and A3 follow the relation $k_1 = k_2 k_3$, where $k_3$ is absolute permeability.41 Following others,13-16 residual saturations are neglected. To relate capillary pressure, $P_c = P_1 - P_2$, to liquid saturation, capillary equilibrium (i.e., Young-Laplace) and a bundle-of-capillaries model are used.41 Capillary pressure-saturation relationships used in this work are identical to those measured by Kusoglu et al.23 A detailed description of mixed-wettability for the cCL and cGDL is found in Balliet et al.18

### Appendix B. Ice-Nucleation-Rate Parameters

In Eqs. 3–5 require independent assessment of the ice/water/substrate triple line contact angle, $\theta$. Since $A$ is independent of $T$, $D(T)$ depends on $\theta$ only through the parameter $B$. From CNT, $B$ is related to the Gibbs-free energy of critical-nucleus formation, $\Delta G^*$, by20,30

$$B(\theta) = \frac{\Delta G^*}{k_B}$$

$$\equiv \frac{4\pi \gamma L^2 \theta^2}{3 \Delta H_{f} k_B T}$$

where $k_B$ is the Boltzmann constant, $\gamma$ is solid/liquid interfacial energy, and $\theta$ is ice specific volume.

From Table I and Eq. B1, similar values of $B$ for BP460/BP800 and a Toray GDL31 suggests that for BP460/BP800 is approximately equal to that of the GDL, or $\theta = 60^\circ$. Unlike BP460/BP800, however, BP120/Vulcan XC72 have significantly decreased ice-nucleation rates (evidenced by larger $B$ in Table I). Values of $B$ are roughly 4 times larger for BP120/Vulcan XC72 than for BP460/BP800, characteristic of an increased contact angle, $\theta$. Eq. B1 demonstrates that $B(T)$ and $\Delta G^*$ increase with $\theta$. Thus, for an increase in $\theta$ from 60$^\circ$ to 110$^\circ$, the increase $B$ decreases from 4 to 0.47. The results in Table I and Eq. B1 indicate that $\Delta G^*$ is a function of $\theta$, with $\Delta G^*$ increasing as $\theta$ decreases.

To investigate further the effect of ionomer coverage on ice nucleation, the Carbon:Nafion mass ratio was varied from 5:2 to 5:8. This result suggests an increase in ionomer coverage, and consequently, an increase in $\Delta G^*$. Thus, for an increase in $\theta$ from 60$^\circ$ to 110$^\circ$, an increase in $B$ results in an increase in ionomer coverage and, similar to BP800 (with 5:2 Carbon:Nafion), a decrease in ionomer coverage and, similar to BP800 (with 5:2 Carbon:Nafion), a decrease in ionomer coverage.

### Table B1. Ice-Nucleation Rate Parameters with Varying Carbon:Nafion Mass Ratio.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon:Nafion Mass Ratio</th>
<th>$A \times 10^{-9}$ (nuclei m$^{-3}$ s$^{-1}$)</th>
<th>$B \times 10^{4}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC72</td>
<td>5:1</td>
<td>13.3</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>5:2</td>
<td>12.0</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>5:4</td>
<td>103.4</td>
<td>41.6</td>
</tr>
<tr>
<td>BP800</td>
<td>5:2</td>
<td>4.6</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>5:4</td>
<td>110.0</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>5:8</td>
<td>305.9</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Figure B1. Calculated dimensionless Gibbs-free energy of critical-nucleus formation, $\Delta G^*/k_BT$, versus dimensionless seed radius, $r^* = R_s/r^*(T)$, for ice/water/substrate contact angles of 60$^\circ$ and 110$^\circ$. The results in Table I and Eq. B1 indicate that $\Delta G^*$ is a function of $\theta$, with $\Delta G^*$ increasing as $\theta$ decreases.

### References