Supplementary Information

Thermoelectrics in Ice Slabs: Charge Dynamics and Thermovoltages

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1 Mathematical justification of two key features in the slow stage

1.1 $\mathcal{O}(d(\Gamma_+ - \Gamma_-)/dt) \sim \mathcal{O}(d(\Gamma_D - \Gamma_L)/dt)$

As discussed in the main text, the net charges at the left half of the ice slab are obtained as

$$e_\pm(\Gamma_+ - \Gamma_-) = P_{b,m}\frac{e_\pm}{e} + E_m\epsilon_0\epsilon_\infty\frac{e_\pm}{e} \tag{S1}$$

$$e_{DL}(\Gamma_D - \Gamma_L) = -P_{b,m}\frac{e_\pm}{e} + E_m\epsilon_0\epsilon_\infty\frac{e_{DL}}{e} \tag{S2}$$

By taking the time derivative of Eq. S1 and S2, we have

$$e_\pm\frac{d(\Gamma_+ - \Gamma_-)}{dt} = \frac{dP_{b,m}}{dt}\frac{e_\pm}{e} + \frac{dE_m}{dt}\epsilon_0\epsilon_\infty\frac{e_\pm}{e} \tag{S3}$$

$$e_{DL}\frac{d(\Gamma_D - \Gamma_L)}{dt} = -\frac{dP_{b,m}}{dt}\frac{e_\pm}{e} + \frac{dE_m}{dt}\epsilon_0\epsilon_\infty\frac{e_{DL}}{e} \tag{S4}$$

In the slow stage, the ionic defect transport weakens the electric field while enhances the polarization field. Because the electric field are positive and polarization field are negative after the pseudo-steady state, the changes of electric and polarization field are all negative corresponding to

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$dP_{b,m}/dt < 0$ and $dE_m/dt < 0$ in Eq. S3 and S4 as shown in Fig. 3d of the main text. Therefore, we have $|e_{DL}d(\Gamma_D - \Gamma_L)/dt| < |e_\pm d(\Gamma_+ - \Gamma_-)dt|$, meaning $|d(\Gamma_D - \Gamma_L)/dt|$ is smaller than $|d(\Gamma_+ - \Gamma_-)/dt|$ or at least at the same order of magnitude.

1.2 $\mathcal{O}(dF_m/dt) \ll \mathcal{O}(dE_m/dt)$

The time derivatives of $P_{b,m}$ and E_m decrease gradually when they approach to the steady state as shown in Fig. 3d in the main text. Therefore, both $P_{b,m}(t)$ and $E_m(t)$ are concave functions to time such that their second derivatives to time are all positive. Now, if we take the time derivative of Eq. S3 and S4, we obtain

$$\begin{aligned} e_\pm \frac{d^2(\Gamma_+ - \Gamma_-)}{dt^2} &= \frac{d^2 P_{b,m}}{dt^2}\frac{e_\pm}{e} + \frac{d^2 E_m}{dt^2}\epsilon_0\epsilon_\infty \frac{e_\pm}{e} \\ e_{DL}\frac{d^2(\Gamma_D - \Gamma_L)}{dt^2} &= -\frac{d^2 P_{b,m}}{dt^2}\frac{e_\pm}{e} + \frac{d^2 E_m}{dt^2}\epsilon_0\epsilon_\infty \frac{e_{DL}}{e} \end{aligned} \tag{S5}$$

where $\frac{d^2 P_{b,m}}{dt^2}$ and $\frac{d^2 E_m}{dt^2}\epsilon_0\epsilon_\infty$ are all positive. Similar to Section 1.1, we have $|e_{DL}d^2(\Gamma_D - \Gamma_L)/dt^2| < |e_\pm d^2(\Gamma_+ - \Gamma_-)/dt^2|$.

Next, integrating the governing equation of the density evolution of a charge carrier i over the ice slab's left half, we have

$$\begin{aligned} \int_0^{W/2} \frac{\partial n_i}{\partial t}\, dx &= \int_0^{W/2} (-\frac{\partial j_i}{\partial x} + G_i + R_i)\, dx \\ \frac{d\Gamma_i}{dt} &= -(j_i|_{W/2} - j_i|_0) + \int_0^{W/2} (G_i + R_i)\, dx \end{aligned} \tag{S6}$$

with $j_i|_0 = 0$ (Eq. 11). The net excesses of H^+ defect over OH^- defect and D defects over L defects in ice slab's left half then follow

$$\frac{d(\Gamma_+ - \Gamma_-)}{dt} = (D_+ - D_-)\frac{dn^0_\pm}{dx}|_{W/2} - (D_+ + D_-)\frac{e_\pm}{k_B T} n^0_{\pm,m}\left(E_m + \frac{\Phi}{e_\pm e_{DL}} P_{b,m}\right) \tag{S7}$$

$$\frac{d(\Gamma_D - \Gamma_L)}{dt} = (D_D - D_L)\frac{dn^0_{DL}}{dx}|_{W/2} - (D_D + D_L)\frac{e_{DL}}{k_B T} n^0_{DL,m}\left(E_m - \frac{\Phi}{e^2_{DL}} P_{b,m}\right) \tag{S8}$$

Now, we multiply Eq. S7 with $e_\pm$ and Eq. S8 with e_{DL} and take the time derivatives of them

$$e_\pm \frac{d^2(\Gamma_+ - \Gamma_-)}{dt^2} = \frac{d}{dt}\left[e_\pm(D_+ - D_-)\frac{dn^0_\pm}{dx}|_{W/2}\right] - \frac{d}{dt}\left[(D_+ + D_-)\frac{e^2_\pm}{k_B T} n^0_{\pm,m}\left(E_m + \frac{\Phi}{e_\pm e_{DL}} P_{b,m}\right)\right] \tag{S9}$$

$$e_{DL}\frac{d^2(\Gamma_D - \Gamma_L)}{dt^2} = \frac{d}{dt}\left[e_{DL}(D_D - D_L)\frac{dn^0_{DL}}{dx}|_{W/2}\right] - \frac{d}{dt}\left[(D_D + D_L)\frac{e^2_{DL}}{k_B T} n^0_{DL,m}\left(E_m - \frac{\Phi}{e^2_{DL}} P_{b,m}\right)\right] \tag{S10}$$

Taking advantage of the fact that the region near ice slab's middle plane is bulk-like, the diffusion terms are time independent and can be eliminated so that Eq. S9 and S10 can be simplified to

$$e_\pm \frac{d^2(\Gamma_+ - \Gamma_-)}{dt^2} = -\frac{d}{dt}\left[e_\pm(D_+ + D_-)\frac{e_\pm}{k_BT}n^0_{\pm,m}\left(E_m + \frac{\Phi}{e_\pm e_{DL}}P_{b,m}\right)\right] \tag{S11}$$

$$e_{DL} \frac{d^2(\Gamma_D - \Gamma_L)}{dt^2} = -\frac{d}{dt}\left[e_{DL}(D_D + D_L)\frac{e_{DL}}{k_BT}n^0_{DL,m}\left(E_m - \frac{\Phi}{e^2_{DL}}P_{b,m}\right)\right] \tag{S12}$$

With $|e_{DL}d^2(\Gamma_D - \Gamma_L)/dt^2| < |e_\pm d^2(\Gamma_+ - \Gamma_-)/dt^2|$, we have the following relationship by introducing $F_m = E_m - P_{b,m}\Phi/e^2_{DL}$ in Eq. S12.

$$\frac{d}{dt}\left|-e_{DL}(D_D + D_L)\frac{e_{DL}}{k_BT}n^0_{DL,m}F_m\right| < \frac{d}{dt}\left|-e_\pm(D_+ + D_-)\frac{e_\pm}{k_BT}n^0_{\pm,m}\left(E_m + \frac{\Phi}{e_\pm e_{DL}}P_{b,m}\right)\right| \tag{S13}$$

Because the ionic defect density is $\sim 10^6$ times smaller than that of Bjerrum defects (i.e. $n^0_{\pm,m} \ll n^0_{DL,m}$), we have

$$\frac{d}{dt}|F_m| \ll \frac{d}{dt}\left|\left(E_m + \frac{\Phi}{e_\pm e_{DL}}P_{b,m}\right)\right| \tag{S14}$$

Here, we replace $P_{b,m}$ with F_m to obtain the relationship of E_m and F_m

$$\frac{d}{dt}|F_m| \ll \frac{d}{dt}\left|\left(E_m + \frac{e_{DL}}{e_\pm}(E_m - F_m)\right)\right| \tag{S15}$$

Based on the absolute value inequality, we have

$$\frac{d}{dt}|F_m| \ll \frac{d}{dt}\left|\left(1 + \frac{e_{DL}}{e_\pm}\right)E_m\right| - \frac{d}{dt}\left|\frac{e_{DL}}{e_\pm}F_m\right| \tag{S16}$$

Move the second term at the right hand side to the left hand side, we obtain

$$\left|\frac{dF_m}{dt}\right| \ll \left|\frac{dE_m}{dt}\right| \tag{S17}$$

2 Derivation of P_m in the slow stage

The derivation of P_m follows the similar approach to that of E_m in the main text. Here, we substitute E_m in Eq. S7 with P_m and F_m.

$$\frac{d(\Gamma_+ - \Gamma_-)}{dt} = -\frac{e}{k_BT_m}\frac{\Phi}{e^2_{DL}}n^0_{\pm,m}(D_+ + D_-)P_{b,m} - \frac{e_\pm}{k_BT_m}n^0_{\pm,m}(D_+ + D_-)F_m + (D_+ - D_-)\frac{dn^0_\pm}{dx}|_{W/2} \tag{S18}$$

Substituting F_m with Eq. S8, we obtain

$$\frac{\frac{d(\Gamma_+-\Gamma_-)}{dt}}{(D_++D_-)\frac{n^0_{\pm,m}}{k_BT_m}}+\frac{\frac{e}{e_{DL}}\frac{d(\Gamma_D-\Gamma_L)}{dt}}{(D_D+D_L)\frac{n^0_{DL,m}}{k_BT_m}}=-\frac{\Phi e}{e^2_{DL}}P_{b,m}(t)-\left[\frac{1-\beta_\pm}{1+\beta_\pm}\frac{\Phi_\pm}{2T_m}-\frac{1-\beta_{DL}}{1+\beta_{DL}}\frac{\Phi_{DL}e_\pm}{2T_me_{DL}}\right]\frac{dT}{dx} \tag{S19}$$

Because $n^0_{DL,m}\sim 10^6 n^0_{\pm,m}$ and $\mathcal{O}(d(\Gamma_+-\Gamma_-)/dt)\sim\mathcal{O}(d(\Gamma_D-\Gamma_L)/dt)$, the second term on the left-hand side of Eq. S19 can be neglected. Substituting Eq. S1 into Eq. S19 we have,

$$\frac{\frac{d}{dt}\left[P_{b,m}+\epsilon_0\epsilon_\infty\left(\frac{\Phi}{e^2_{DL}}P_{b,m}+F_m\right)\right]}{e^2(D_++D_-)n^0_{\pm,m}}=-\frac{\Phi e}{e^2_{DL}}P_{b,m}(t)+\left[\frac{1-\beta_\pm}{1+\beta_\pm}\frac{\Phi_\pm}{2T_m}-\frac{1-\beta_{DL}}{1+\beta_{DL}}\frac{\Phi_{DL}e_\pm}{2T_me_{DL}}\right]\frac{dT}{dx} \tag{S20}$$

Because $\mathcal{O}(dF_m/dt)\ll\mathcal{O}(dE_m/dt)$ and $F_m=E_m-P_{b,m}\Phi/e^2_{DL}$, we have
$\mathcal{O}(dF_m/dt)\ll\mathcal{O}(\Phi/e^2_{DL}dP_{b,m}/dt)$. Therefore, the F_m term in Eq. S20 can be neglected.

$$\frac{\left(\epsilon_0\epsilon_\infty+\frac{e^2_{DL}}{\Phi}\right)k_BT_m}{e^2(D_++D_-)n^0_{\pm,m}}\frac{dP_{b,m}(t)}{dt}=-P_{b,m}(t)+\frac{e^2_{DL}}{\Phi}\left[\frac{1-\beta_\pm}{1+\beta_\pm}\frac{\Phi_\pm}{2T_m}-\frac{1-\beta_{DL}}{1+\beta_{DL}}\frac{\Phi_{DL}e_\pm}{2T_me_{DL}}\right]\frac{dT}{dx} \tag{S21}$$

Due to the much larger time scale in slow stage compare to that in fast stage, the initial condition for Eq. S21 can be approximated as $P_b(t=0)=P_{b,m,f}=-\epsilon_0\epsilon_\infty E_{m,f}$ so that we have

$$P_{b,m}(t)=(-\epsilon_0\epsilon_\infty E_{m,f}-P_{b,m}(t=\infty))e^{-t/\tau_{P_b,s}}+P_{b,m}(t=\infty) \tag{S22}$$

The steady state polarization density field at ice slab's middle plane is

$$P_{b,m}(t=\infty)=-\frac{e_{DL}}{2e\Phi T_m}\left[\frac{1-\beta_\pm}{1-\beta_\pm}\Phi_\pm e_{DL}-\frac{1-\beta_{DL}}{1-\beta_{DL}}\Phi_{DL}e_\pm\right]\frac{\Delta T}{W} \tag{S23}$$

Here, we notice the time scale for $P_{b,m}(t)$ to reach the steady state is same to that of $E_m(t)$

$$\tau_{P_b,s}=\tau_{E,s}=\frac{k_BT_m\left(\epsilon_0\epsilon_\infty+\frac{e^2_{DL}}{\Phi}\right)}{e^2(D_++D_-)n^0_\pm}=\left(1+\frac{e^2_{DL}}{\Phi\epsilon_0\epsilon_\infty}\right)\frac{e^2_\pm}{e^2}\frac{\lambda^2_\pm}{(D_++D_-)/2} \tag{S24}$$

3 Literature values for defect properties in ice

The properties of point defects in ice reported in literature are presented in Table S1. The corresponding temperature at which a property was reported is shown, except for that of activation and migration energy, which is generally assumed to be insensitive to temperature.

Table S1: Properties of defects in ice from different sources.

	Value	Note	Ref.		Value	Note	Ref.
μ_+	7.5×10^{-6} $m^2/(V\cdot s)$	273 K	1	μ_D	negligible	253 K	2
μ_+	2.7×10^{-8} $m^2/(V\cdot s)$	273 K	3	$\Phi_\pm$	1.2±0.1 eV	–	4
μ_+	9.2×10^{-8} $m^2/(V\cdot s)$	240 K	5	$\Phi_\pm$	0.96±0.13 eV	–	1
μ_+	1×10^{-7} $m^2/(V\cdot s)$	253 K	2	$\Phi_\pm$	1 eV	–	6
μ_-	$7.5\times10^{-8\sim-7}$ $m^2/(V\cdot s)$	263 K	1	$\Phi_\pm$	⩾1.4 eV	–	2
μ_-	2.7×10^{-8} $m^2/(V\cdot s)$	240 K	5	Φ_{DL}	0.68±0.04 eV	–	4
μ_-	3×10^{-8} $m^2/(V\cdot s)$	253 K	2	Φ_{DL}	0.664 eV	–	3
μ_+/μ_-	10.0	253 K	7	Φ_{DL}	0.790±0.082 eV	–	8
μ_L	1.16×10^{-8} $m^2/(V\cdot s)$	253 K	4	Φ_{D_+}	$\sim$ 0 eV	–	8
μ_L	2×10^{-8} $m^2/(V\cdot s)$	263 K	9	Φ_{D_+}	-0.22 eV	–	10
μ_L	5×10^{-8} $m^2/(V\cdot s)$	273 K	3	Φ_{D_L}	0.235±0.010 eV	–	4
μ_L	2×10^{-8} $m^2/(V\cdot s)$	253 K	2	Φ_{D_L}	0.190±0.017 eV	–	8
μ_D	$\leqslant \mu_L$	253 K	4	Φ_{D_L}	0.292 eV	–	3
μ_D	$\leqslant \mu_L$	263 K	9	Φ_{D_L}	0.235 eV	–	6

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