Reversible heating in electric double layer capacitors

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A detailed comparison is made between different viewpoints on reversible heating in electric double layer capacitors. We show in the limit of slow charging that a combined Poisson-Nernst-Planck and heat equation, first studied by d’Entremont and Pilon [J. Power Sources 246, 887 (2014)], recovers the temperature changes as predicted by the thermodynamic identity of Janssen, Härtel, and van Roij [Phys. Rev. Lett., 113, 268501 (2014)], and disagrees with the approximative model of Schiffer, Linzen, and Sauer [J. Power Sources 160, 765 (2006)] that predominates the literature.

With the relation between heat and entropy formulated by Clausius in 1855, and with the establishment of the importance of ion entropy to the electric double layer (EDL) by Gouy (1910) and Chapman (1913)[1], almost a century still passed before reversible, adiabatic heating and cooling was measured in electric double layer capacitors (EDLCs)[2]. Unlike irreversible Joule heating, occurring everywhere in the electrolyte when an EDLC is charged at finite currents, it turns out that the sources of reversible heating are located only within the nanometer-range vicinity of the electrode’s surface. One therefore needs EDLCs whose surface-to-volume ratio is as high as possible to notice an appreciable reversible temperature variation. This has become possible and relevant in recent years because electrodes can now be manufactured from porous carbon with internal surface areas up to 2000 m$^2$g$^{-1}$. Electrolyte-filled supercapacitors made from these electrodes are characterized by a high capacitance, fast (dis)charging rates, and high cyclability[3]. These favorable properties have sparked a huge scientific interest in supercapacitors in recent years. In fact supercapacitors have already been used in airplanes and busses, and they are suggested for energy generation[4–7] and capacitive deionization[8]. The performance of supercapacitors for energy storage usually suffers, however, from increased temperatures causing aging of materials, increased internal resistance, decreased capacitance, parasitic electrochemical reactions, and self discharging[9][11]. Efforts were therefore made both in experiments[2][10][13] and modeling[14][16] to gain insight in the thermal behavior of supercapacitors. However, a unified understanding of reversible heating effects occurring during EDL buildup is still lacking. This Letter for the first time quantitatively reconciles two viewpoints on reversible heating. Within the thermodynamic viewpoint, two distinct identities for isentropic processes are discussed, only one of which (we show) agrees with the other, kinetic viewpoint.

For the thermodynamic viewpoint, consider an EDLC on which a potential is imposed by connecting it to a battery. The electrodes then obtain surface charges which are screened by diffuse clouds of counter ionic charge (see Fig.1). This EDL buildup is characterized by a decrease of the ionic configuration entropy. For a thermally insulated capacitor that is charged quasi-statically, thermo-dynamics demands via the Second Law ($dS = 0$) that this decrease is counterbalanced by an electrolyte entropy increase: the EDLC heats up. Upon quasi-static adiabatic discharging the opposite happens: while the EDL breaks down the electrolyte cools. Experimental observations of reversible heating in an EDLC were first reported in[2] (and later in[12][13]). Here, the EDL buildup was described theoretically as an isentropic compression of an ideal gas. While this model correctly captures the exchange between configuration and momentum contributions to the fixed phase space volume, it completely ignores the long-range Coulomb interactions among the constituent particles. An alternative expression not hinges on ideal-gas reasoning was proposed by the current authors in[5] (and repeated here in Eq. (2)). Interestingly, there are many examples of isentropic temperature changes which are governed by equations structurally similar to our Eq. (2) below, e.g. the magnetocaloric[17], the electrocaloric[18], and the Joule-Gouge effect [19].

The kinetic viewpoint on exchange between heat and electric energy in the EDL can be traced back (at least) to Verwey and Overbeek[20] who stated for EDL discharging that “...the counter ions must diffuse more and more back into the solution. This diffusion occurs against electric forces... The energy needed to raise the electric energy of these ions must be taken up from the surrounding ions and molecules, and is delivered as kinetic energy from the thermal motion of the latter.” A thermally ins-
sulated EDLC therefore cools upon discharging. This exchange between electric energy and heat is captured in the internal energy balance (see Eq. (1)) as the inner product \( \mathbf{I} \cdot \mathbf{E} \) of the ionic current \( \mathbf{I} \) and the electric field \( \mathbf{E} \) [21, 23]. In bulk electrolytes ions respond Ohmically to an imposed electric field (see Eq. (1)): the electric field drives a current that is proportional to and aligned with this field. Hence \( \mathbf{I} \cdot \mathbf{E} \sim I^2 > 0 \) in the bulk, such that electric energy is irreversibly transferred to the internal energy of the fluid, also known as Ohmic losses or Joule heat. In general, however, the direction of particle fluxes is set by the gradient of the electrochemical potential, which, next to the gradient in electric potential, also contains the gradient of the local ion density. In regions of strong concentration gradients in which local electroneutrality is broken it is therefore possible that the ionic current opposes the electric forcing (\( \mathbf{I} \cdot \mathbf{E} < 0 \)), giving rise to localized cooling. Such a cooling effect is therefore hypothesized in the vicinity of electrodes (not only ideally polarizable [14] but also harboring electrochemical reactions [23]), as well as near ion exchange membranes [24]. Since the sources of the reversible heating are located only in the EDL, the resulting temperature variations are more pronounced in nanoporous supercapacitors that have a large surface-to-volume ratio. However, while supercapacitors have a highly intricate pore structure, this Letter focuses for illustration purposes on a parallel plate EDLC as it already captures the essential physics. With the ionic currents captured within a modified Poisson-Nernst-Planck model, we show that the heat equation recovers the prediction of Eq. (2) in the limit of slow charging, thereby reconciling the thermodynamic and kinetic viewpoints. The ideal-gas reasoning that is often used for illustration purposes [9, 11, 14], or even to fit to experiments [13, 15], cannot reproduce the adiabatic temperature change.

Consider a thermally insulated container with two planar parallel electrodes separated by an (incompressible) 1:1 electrolyte of dielectric constant \( \epsilon_d \) (Fig. 1). The electrolyte consists of \( 2N = N_+ + N_- \) ions and \( N_s \) solvent (s) molecules, and occupies a volume \( V_{\text{el}} = AL \) where \( L \) is the electrode separation, and \( A \) the surface area of each of the electrodes. An external battery imposes the potential \( \Psi \) and \( -\Psi \) to the ideally polarizable electrodes, leading to opposite surface charges \( Q \) and \( -Q \) with corresponding surface charge densities \( \pm e \sigma = \pm Q/A \), where \( e \) is the proton charge. The coordinate \( z \) runs perpendicular to the plates from \( z = 0 \) to \( z = L \). At finite potential differences, the density profiles \( \rho_\pm(z) \) are not homogenous since an inhomogeneous EDL is formed to screen the surface charge. We take the limit \( A \to \infty \) so that edge effects can be ignored. The bulk salt concentration is defined in the uncharged state as \( \rho_0 = N/V_{\text{el}} \). Since the dielectric constant \( \epsilon_d(T, \rho_0) \) depends in general on both \( T \) and \( \rho_0 \), the Bjerrum length \( \lambda_B = e^2/\epsilon_d k_B T \), with \( k_B \) the Boltzmann constant, could vary through the system. We choose to ignore this (usually weak) dependence henceforth and focus on aqueous electrolytes at fixed \( \epsilon_d \). Moreover, we ignore convection fluid flow and assume a fixed atmospheric pressure \( p \), although we do not write \( p \) as an explicit variable in most expressions.

An approximate expression for the reversible temperature rise upon electrode charging was proposed in [2] where the adiabatic EDL buildup was described as the isentropic compression of \( 2N \) ideal-gas particles, from the complete electrolyte volume \( V_{\text{el}} = AL \) to two microscopic layers (one for each ion species) of thickness \( \lambda \) and volume \( V_{\lambda} = A \lambda \). The reversible temperature rise, from the initial low temperature \( T_L \) to the final high temperature \( T_H \), is then easily found by evaluating the total differential of the entropy \( S(T, \rho) \), depending here on the volume \( \rho \) that varies between \( \rho_{\text{el}} \) and \( \rho_{\lambda} \), which results in

\[
\ln \frac{T_H}{T_L} = \frac{2N k_B}{\rho c_p V_{\lambda}} \ln \frac{L}{\lambda},
\]

where we write the specific heat capacity at a general fixed variable \( x \) as \( c_p \equiv T (\partial S/\partial T)_x / \rho V_{\lambda} \) with \( \rho \) the electrolyte mass density. The authors of [2] manually inserted EDL characteristics via a Helmholtz model where the number \( N' = N_H \) ions involved in the adsorption process scales linearly with the surface charge as \( N_H = Q/e = A \sigma \). Moreover, these ions are confined to a layer of fixed width independent of temperature and salt concentration. A first step towards the inclusion of ion interactions can be made by employing Gouy-Chapman results instead. The number of adsorbed ions is then \( N' = N_{\text{GC}} \), with \( N_{\text{GC}}/A = \sqrt{\sigma^2 + \sigma^2 - \sigma} \), where \( \sigma = \sqrt{2 \rho_0 / \pi \lambda_B} \), and the EDL size is characterized by the Debye length \( \lambda = \lambda_D \equiv \sqrt{8 \pi \rho_0 \lambda_B}^{-1} \), i.e. \( \lambda \) in Eq. (1) does not depend on \( T \) and \( \rho_0 \) [23]. Moreover, \( \rho_0 \) itself depends on the surface charge since the relation \( N = \rho_0 V_{\lambda} + N' \) needs to be obeyed for canonical (fixed \( N \)) charging. Due to the limitations of the ideal-gas treatment, we now describe the EDLC in terms of the macroscopic variables temperature, charge and potential from the start. The entropy \( S(T, Q) \) is then a function of the independent variables \( Q \) and \( T \). The potential is not an independent variable since it is determined uniquely by the Poisson equation at given \( Q \) and \( T \). Since no heat \( \delta Q \) flows through the adiabatic walls of our system, the First Law of thermodynamics \( dU = \delta Q + \delta W \) simplifies and the internal energy is solely affected by electrostatic work \( \delta W \) performed on the system by the external battery, hence \( dU = \delta W = 2\Psi dq \). The temperature change due to an isentropic change of surface charge now follows from the total differential \( dS(T, Q) = 0 \). Employing a Maxwell relation we find

\[
d\ln T = \frac{2}{\rho c_p Q} \left( \frac{\partial \Psi}{\partial T} \right)_Q \, ed\sigma.
\]

For aqueous electrolytes at moderate ion concentration the heat capacity of the water molecules dwarfs the heat capacity of the ions. At isobaric conditions this means \( c_Q \approx c_p \), with \( c_p \) the specific heat capacity of the solvent.
As \((\partial \Psi / \partial T)\), in general depends non-trivially on both \(Q\) and \(T\), we need to integrate Eq. (2) numerically, from a relation between the macroscopic observables \(\Psi\) and \(Q\) for a given electrode/electrolyte system, which can involve experiments \([9]\), simulations \([20]\), or a microscopic model \([27]\). In this Letter we capture the EDL within classical density functional theory (DFT). While much effort has been devoted to the development of highly accurate functionals for the EDL (see \([28]\) and references therein), for the illustrative purpose of the present Letter it suffices to use a relatively simple grand potential functional \(\Omega(\rho_\pm, \sigma)\), which reads in the planar geometry of interest

\[
\beta \Omega = A \sum_{\alpha=\pm} \int_0^L dz \left\{ \rho_\alpha(z) \left[ \ln \rho_\alpha(z) \Lambda^3_\alpha - 1 - \beta \mu_\alpha(z) \right] + \rho_w(z) \left[ \ln \rho_w(z)v - 1 + \frac{1}{2} \phi(z)q(z) \right] \right\}. (3)
\]

The first line is the ideal-gas grand potential of ions at chemical potential \(\mu_\pm\), with \(\Lambda_\pm\) the ionic thermal wavelength. The first term of the second line captures steric hindrance qualitatively and is based on a lattice gas model of equal-sized solvent molecules and ions where an upper limit \(1/v\) is imposed on the local density (which cannot exceed close packing) via the constraint \(\rho_\pm(z) + \rho_\mp(z) + \rho_w(z)v = 1\) \([29]\), with \(\rho_w\) the water density and \(v\) the hydrated ionic volume. Finally, the last term in Eq. (3) is the mean-field electrostatic energy, with \(\phi(z) = \rho_\pm(z) - \rho_\mp(z) + \sigma (\delta(z) + \delta(z - L))\) the local unit charge density, and \(\phi(z) = e\bar{\psi}(z)/k_B T\) the local dimensionless electrostatic potential, governed by Poisson's law

\[
\epsilon_d \partial^2 z \bar{\psi}(z) = -4\pi e [\rho_\pm(z) - \rho_\mp(z)], \quad 0 < z < L. (4)
\]

The boundary conditions \(\beta \partial_z \bar{\psi}(z)|_{z=0,L} = -4\pi \lambda_B \sigma\) imposed at the electrodes’ surfaces follow from Gauss’ law. From the Euler-Lagrange equations \(\delta \Omega/\delta \rho_\pm(z) = 0\) follows the electrochemical potential

\[
\tilde{\mu}_\pm(z) = k_B T \ln \frac{\rho_\pm(z) \Lambda^3_\pm}{1 - v[\rho_\pm(z) + \rho_\mp(z)]} \pm \epsilon \psi(z), (5)
\]

which for future reference we split up as \(\tilde{\mu}_\pm \equiv \mu_\pm \pm \epsilon \psi\) into the chemical potentials \(\mu_\pm\), including contributions from all non-electric interactions, and an electric contribution \(\epsilon \psi\). Demanding in equilibrium the electrochemical potential \(\mu_\pm(z)\) to be a spatial constant, we can solve Eq. (5) analytically for the potential dependence of the density profiles to find modified Boltzmann distributions. Equation (4) can then be closed yielding the so-called modified Poisson-Boltzmann equation \([30]\), which we solve at a set of temperatures and fixed \(\sigma\) to extract the temperature dependence of the surface potential \(\Psi = \psi(z = 0)\). One then evaluates \((\partial \Psi / \partial T)\) to solve Eq. (2) for \(T_H\).

We turn the discussion to charging dynamics where a time-dependent surface potential \(\Psi(t)\) drives the system out of equilibrium. As a result, the densities \(\rho_\pm(z,t)\) and electrostatic potential \(\psi(z,t)\) are now time dependent. Moreover, out of equilibrium, the electrochemical potential of Eq. (5) is not a spatial constant. Consequently, the Poisson equation (which still holds because the electromagnetic field responds instantaneously to the comparatively slow ions) is no longer closed by the Boltzmann weights. We use dynamical density functional theory (DDFT) to obtain the particle currents from the electrochemical potentials \(J_\pm = -D \rho_\pm \beta \partial_z \tilde{\mu}_\pm\). The diffusion constant \(D\) is assumed constant and identical for cations and anions, and for notational clarity the argument \((z,t)\) is dropped. The ion densities can now be found from the continuity equation, to give the Nernst-Planck equation

\[
\partial_t \rho_\pm = D \partial_z (\rho_\pm \beta \partial_z \tilde{\mu}_\pm), (6)
\]

with blocking boundary conditions \(J_\pm|_{z=0,L} = 0\) at the electrodes. The ionic conduction current \(I \equiv e (J_+ - J_-)\) amounts to

\[
I = - D e \left\{ \partial_z q + (\rho_+ - \rho_-) \beta e \partial_z \psi + q \partial_z \ln [1 - v(\rho_+ + \rho_-)] \right\}. (7)
\]

This equation shows that in bulk \((q = 0)\) the electric field \(-\partial_z \psi\) drives an ionic current \(I\) subject to an ionic resistivity \(\sigma = k_B T / De^2(\rho_+ + \rho_-)\). Crucial to the reversible heat effect is that the EDL \((\partial_\psi q \neq 0)\) can support ionic currents that oppose the local electric field.

To find the temperature profiles \(T(z,t)\) we follow \([21]\) and define the local specific internal energy \(u \equiv U/\rho V_D\) as the energy associated with thermal agitation and all short ranged (non-electrostatic) particle interactions. The internal energy balance is then given as

\[
\partial_t u = -\partial_z J_q + IE. (8)
\]

Here, the heat flow \(J_q = -k_B T \sum_i \tilde{H}_i J_i\) contains Fourier heat diffusion (with heat conductivity \(k\)), and the partial molecular enthalpy \(\tilde{H}_i = T^2 (\partial (\mu_i/T)/\partial T)_{\rho,V_D}\) carried by particle currents, with \(i,i' = \{+, -, s\}\) (see \([32]\) and Appendix A for details). In \(J_q\) we did not include a Dufour term \(\sim \nabla \mu\), which is consistent with our disregarding Soret terms \(\sim \nabla T\), the reciprocal phenomenon, in Eq. (6) \([33]\). Equation (8) is rewritten in Appendix B into the heat equation

\[
\partial_t \rho_\pm \tilde{H}_i = k \partial^2 T + \tilde{\epsilon}_{rev} + \tilde{\epsilon}_{urr}, (9)
\]

where the \((ir)\)reversible heating rates \(\tilde{\epsilon}_{urr} \equiv I r^2 T\) and \(\tilde{\epsilon}_{rev} \equiv I r De \left\{ \partial_z q + q \partial_z \ln [1 - v(\rho_+ + \rho_-)] \right\}\) both stem from the ‘total heating rate’ \(IE = \tilde{\epsilon}_{urr} + \tilde{\epsilon}_{rev}\) in Eq. (8). Note that \(\tilde{\epsilon}_{rev}\) only has a non-zero contribution in the EDL where \(q \neq 0\). Moreover, within this region the fraction \(\tilde{\epsilon}_{urr}/\tilde{\epsilon}_{rev} \sim 1/\partial_z q \to 0\) for slow charging \((I \to 0)\). Equations (4)-(7) and (9) form a closed set which we refer to as \(\text{PNPh}\) for Poisson, Nernst-Planck, and heat. Numerical results for the \((z,t)\)-dependence of
\(\varphi, \rho_\perp, q, J_\perp, I,\) and \(T\) were obtained for an (initially uncharged) EDLC of plate separation \(L = 50\) nm at \(T = 20^\circ\text{C}\), filled with an aqueous NaCl electrolyte at \(\rho_0 = 0.3\) nm\(^{-3}\). We use the following parameter set for this electrolyte: \(v = 0.16\) nm\(^3\) (from \(\mathbb{M}\)), \(D = 1.6 \cdot 10^{-9}\) m\(^2\) s\(^{-1}\), \(\kappa = 0.599\) W m\(^{-1}\) K\(^{-1}\), \(\epsilon = 71,\) \(\varrho = 989.3\) kg m\(^{-3}\), \(c_p = 4.182\) kJ K\(^{-1}\) kg\(^{-1}\). We start with the uncharged EDLC at \(T_k = 20^\circ\text{C}\) and ramp the electrode potential linearly from \(\varphi = 0\) to \(\varphi = 10\) during a time interval \(10\tau\) (Fig. 2(a), inset), with time measured in units of the ‘RC-time’ \(\tau_c = \lambda_D L/D\). For the slow charging rates \(\tau/\tau_c = \{5, 100\}\) considered, the temperature \(T(z, t)\) is practically homogenous throughout the cell. With \(\varphi(t)\) and \(T(z, t)\) at hand we eliminate the time dependence of the latter. The black dotted lines in Fig. 2(a) then represent the measurement \(\Delta T(\sigma) = T(z = 0, \sigma) - T_k\). We also plot the adiabatic temperature rise as predicted by the thermodynamic identities Eq. (1) for both the Helmholtz and Gouy-Chapman adsorption models (blue dashed), and Eq. (2) (red). For the slow charging process at \(\tau/\tau_c = 100\) we see a near-perfect agreement between the temperature rise predictions of Eq. (2) and the PNPh equations. Equation 1 does not preform as well. This is numerical evidence for our claim that Eq. (2) and not Eq. (1) captures the thermodynamics of EDLCs. In Fig. 2(b) we show the total heating rate \(IE\) half-way (\(t/\tau = 5\)) through the charging process with \(\tau/\tau_c = 5\). The corresponding instantaneous anion (dotted), cation (dashed) and charge density profiles (red) are shown in Fig. 2(b) (inset). For comparison we also consider the reversed process, starting at an equilibrated state at \(\varphi = 10\) and discharging to \(\varphi = 0\) at the same charging rate \(\tau/\tau_c = 5\). The negative of the heating rate half-way through this discharging process is indicated with a dotted line in Fig. 2(b). The heating rates \(IE\) exhibit a clear peak associated with \(\dot{q}_{\text{rev}}\) in the EDL where the charge density \(q\) is non-vanishing. Towards the bulk only the small contribution \(q_{\text{rev}}\) persists. Upon decreasing the (dis)charging rates, this strictly-positive Joule heating gets progressively smaller, and the (dis)charging heating rates turn into mirror images of one another (not shown).

This Letter discusses reversible heating in EDLCs from two different viewpoints. On the one hand we considered the heat equation, which was derived decades ago for general settings [21]. Only recently [14] it was specified to the case of adiabatic EDLC charging, where particle currents were found from Poisson-Nernst-Planck equations. In [14] this model was shown to quantitatively reproduce the reversible temperature oscillation as observed in supercapacitors [2]. Within this PNPh model cooling is understood as the consequence of ionic currents following the gradient of electrochemical potential but opposing the local electric field. Since this only occurs in the EDL, the reversible heating effect is highly localized (see Fig. 2(b)). While the level of sophistication of the PNPh model sufficed for the purposes of the current Letter (large plate separation, slow charging hence small spatial temperature variation), when considering fast (dis)charging of nanoporous supercapacitors the adiabatic approximation underlying DDFT becomes less justifiable. Moreover, when spatial variations in the diffusion constant and temperature become non-negligible, the use of a free energy functional is problematic, as in DFT the temperature enters as an externally imposed (spatially constant) parameter. Future work could build on recent developments that address these problems [35][37].

The other, thermodynamic, viewpoint, brought forth two distinct identities (Eqs. (1) and (2)) for the temperature change upon isentropic charging of EDLCs. Compared to the PNPh model, the merits of Eq. (2) are twofold. Firstly, its simplicity facilitates easy interpretation. Reversible temperature changes are controlled essentially by a small set of parameters \(\{\sigma, \varrho c_p, L\}\) together with a system-dependent derivative \((\partial \Psi / \partial T)_Q\). The sec-

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**Figure 2.** (color online) (a) The temperature increase \(\Delta T\) upon adiabatic charging of two electrodes separated by \(L = 50\) nm, starting at uniform salt concentration \(\rho_0 = 0.3\) nm\(^{-3}\), and a low temperature \(T = 20^\circ\text{C}\). Plotted are data obtained from Eq. (1) (blue dashed) with \(\lambda = \lambda_D\) for both Helmholtz and Gouy-Chapman adsorption, Eq. (2) (red), as well as the PNPh system (black dotted) with a linear voltage ramp (inset) of inverse slope \(\tau/\tau_c = \{5, 100\}\). (b) The total heating rate (line) within the immediate vicinity of the electrode, halfway (\(t/\tau = 5\)) through the \(\tau/\tau_c = 5\) charging process of (a). The inset shows the corresponding instantaneous anion (line), cation (dashed) and charge density profiles (red dotted). The mirror discharging process at the same time and charging rate is also plotted (dotted).
ond merit of Eq. (2) is that, as a thermodynamic identity, it does not rely on uncontrolled approximations, and can be used as a reliable predictor for the lower bound of temperature variations. Approximations enter the theory at the level of \((\partial \Psi / \partial T)_Q\), so that more accurate estimates can be found by systematically improving the grand potential Eq. (3), by including for instance solvent polarizability \([25]\), a better description of excluded volume interactions \([24]\), and residual ion correlations \([28]\) (see also Appendix C).

While oversimplified ideal-gas reasoning permeates the reversible heating literature \([9, 11, 13–15]\), the main finding of this Letter is that the thermodynamic identity Eq. (2), and not Eq. (1), constitutes the slow charging limit of the PNPh system. The kinetic and thermodynamic viewpoints give complementary information that together allow for a more complete understanding of reversible temperature variation in EDLCs. While oversimplified ideal-gas reasoning permeates the reversible heating literature \([9, 11, 13–15]\), the main finding of this Letter is that the thermodynamic identity Eq. (2), and not Eq. (1), constitutes the slow charging limit of the PNPh system. The kinetic and thermodynamic viewpoints give complementary information that together allow for a more complete understanding of reversible temperature variation in EDLCs.

Using the total differential of the entropy (employing a Maxwell identity and identifying the heat capacity \(C_p\)),

\[
dS = \frac{C_p}{T} dT + \left(\frac{\partial V}{\partial T}\right)_{p,N} dp - \sum_i \left(\frac{\partial \mu_i}{\partial T}\right)_{p,N_i} dN_i,
\]

we eliminate \(dS\) in Eq. (A2) in favor of \(dT\) to find

\[
dH = C_p dT + \left[ V - T \left(\frac{\partial V}{\partial T}\right)_{p,N} \right] dp
+ \sum_i \left[ \mu_i - T \left(\frac{\partial \mu_i}{\partial T}\right)_{p,N_i} \right] dN_i.
\]

The partial molecular enthalpy Eq. (A1) then reduces to the so-called partial Gibbs-Helmholtz equation

\[
\tilde{H}_i = \mu_i - T \left(\frac{\partial \mu_i}{\partial T}\right)_{p,N_i} = -T^2 \left(\frac{\partial \mu_i^s}{\partial T}\right)_{p,N_i},
\]

with \(i' = \{+, -, s\}\). Since our system of interest is not homogenous, one should instead consider a subspace region of volume \(V\) occupied by \(N_i\) particles of each of the \(i\) species. This region should be small enough so that \(\rho_i = N_i/V\) is the locally homogenous particle density. One could then repeat the above exercise to find the partial molecular enthalpy \(\tilde{H}_i \equiv \left(\partial H/\partial N_i\right)_{T,p,N_{i\neq i}}\), defined in terms of the enthalpy \(H(S,p,N_{\mu\neq i},N_i)\) within this space region, to find the same expression Eq. (A5) in terms of the \(\zeta\)-dependent chemical potential. Inserting the ionic chemical potential (first part of Eq. (5)) into Eq. (A5) then gives

\[
\tilde{H}_i = -\frac{3}{2} k_B T + \frac{k_B T}{1-v(\rho_+ + \rho_-)} \left(\frac{\partial \ln V}{\partial \ln T}\right)_p.
\]

were we used that \(\Lambda_1 \sim 1/\sqrt{T}\). Interestingly, the first term in Eq. (A6) that appears is the ideal-gas energy, and not the ideal-gas enthalpy. If all species \(i\) had been treated at the ideal-gas-level (with \(v = 0\)), then one should have substituted \(\rho_i = pk_BT\) in Eq. (5), which would have led to the ideal-gas enthalpy \(\tilde{H}_i = 5k_BT/2\). However, adding ions (see Eq. (A1), the volume they explore does not grow as an ideal gas at fixed pressure as \(V \sim N_{\mu}\), instead \(V\) stays roughly unaffected because it is primarily determined by the solvent molecules, which are markedly nonideal.

In the second term of Eq. (A6) we recognize \((\partial \ln V/\partial \ln T)_p = \alpha T\) with \(\alpha\) the volumetric expansivity \(\alpha = (\partial \ln \theta/\partial T)_p\) of the fluid at mass density \(\theta\). In the bulk electrolyte, the volume \(V\) is predominantly occupied by water molecules, so that we can interpret the volumetric expansivity of the fluid with that of pure water. At \(20^\circ C\) this amounts to \(\alpha T = 0.06\) \([13]\). The second term in Eq. (A6) therefore only gives a small correction to the first term, and is often disregarded \([14]\).

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**Appendix A: Partial molecular enthalpy**

The partial molecular enthalpy \(\tilde{H}_i\) of component \(i = \{+, -, s\}\) is defined for homogeneous systems in terms of the enthalpy \(H(S,p,N_{\mu\neq i},N_i)\) as

\[
\tilde{H}_i = \left(\frac{\partial H}{\partial N_i}\right)_{T,p,N_{i'\neq i}},
\]

which is related to the partial molar enthalpy (common in chemistry literature) by division by Avogadro’s number. In the main text we defined the internal energy as the kinetic energy and microscopic interaction energy of the constituent particles without electric contributions, which is in line with \([21, 22]\). With this choice, \([21, 22, 42]\) argue that it is the chemical potential, and not the electrochemical potential that enters the Gibbs relation and therefore also in the total differential of the enthalpy

\[
dH = Ts + V dp + \sum_i \mu_i dN_i.
\]
As opposed to the dilute bulk, at high electric potentials Eq. \((A6)\) is problematic in the EDL. Interpreting the coefficient of thermal expansivity \(\alpha\) with that of pure water does not hold here because of high local ion densities. Moreover, an artifact of the lattice gas free energy functional Eq. \((B3)\), the steric interactions are thermal (do not depend on temperature). This is also reflected by the fixed lattice spacing \(v^{1/3}\) which erroneously gives \(\partial (\ln V)\partial (\ln T)\) always. Meanwhile, the vanishing of the term \(\partial (\ln V)\partial (\ln T)\) is at high electric potentials accompanied by a divergence of its prefactor \(k_BT/(1-v(\rho_+ + \rho_-))\). More explicit solvent modeling might be necessary to get a better grip on the thermal expansivity term of \(H_i\) in the EDL region.

Appendix B: Derivation heat equation

We follow Refs. [21, 22, 23] to sketch the derivation of the heat equation from the internal energy balance Eq. \((B3)\). We write the total mass of component \(i\) as \(m_i = N_iM_i\), with \(M_i\) the molecular weight, such that the total mass is \(m = m_+ + m_- + m_s\) such that the electrolyte mass density is \(\vartheta = m/V_0\). The enthalpy \(H(S,p,N_+,N_s)\) can then be written in terms of the total mass of the individual components \(H(m_+,m_-,...,m_s)\). Euler’s theorem then allows us to write the enthalpy in terms mass fractions \(c_\pm = m_\pm/m\) as \(H(m_+,m_-,...,m_s) = mh(c_+,c_-)\), with \(h\) the specific enthalpy density, the total differential of which reads

\[
\rho \frac{dh}{dt} = \rho \left( \frac{\partial h}{\partial T} \right)_{p,c_k} \frac{dT}{dt} + \rho \left( \frac{\partial h}{\partial p} \right)_{T,c_k} \frac{dp}{dt} + \sum_k \rho \left( \frac{\partial h}{\partial c_k} \right)_{T,p,c_k} \frac{dc_k}{dt},
\]

with \(k = \{+,-\}\). For the last term Ref. [21] (p. 458) and Ref. [23] (p. 609) provide alternative derivations both yielding

\[
\left( \frac{\partial h}{\partial c_k} \right)_{T,p} = \frac{H_k}{M_k} - \frac{H_s}{M_s}.
\]

The left hand side of this equation we can also express, via \(gh = g\rho + p\) and Eq. \((B3)\), as

\[
\rho \partial_t h = -\partial_x J_q + \partial_x p + IE.
\]

Combination of Eqs. \((B4)\) and \((B5)\), and inserting the heat flow, \(J_q = -\partial_x T + \sum_i H_i \partial_x J_i\), then gives

\[
\varrho c_p \partial_t T = \kappa \partial_x^2 T + IE + \alpha T \partial_x p - \sum_i J_i \partial_x H_i.
\]

Here, the electric field is found via Eq. \((A7)\) as

\[
E = I_\varphi + r \partial_x \left( \partial_x q + q \partial_x \ln \left[ 1 - v(\rho_+ + \rho_-) \right] \right).
\]

The term \(IE\) then gives the (ir)reversible heating rates \(\dot{\alpha}_{irr} = I^2 r\) and \(\dot{\alpha}_{rev} = I r \partial_x \{ q + q \partial_x \ln \left[ 1 - v(\rho_+ + \rho_-) \right] \}\).

As discussed above, the term \(\alpha \equiv \partial (\ln g)/(\partial T)\) in Eq. \((B6)\) is the (usually small) volumetric thermal expansivity of the electrolyte. Also \(\partial_x p\) is small since our (incompressible) liquid is isobaric throughout the cell, and from here on we therefore drop the term \(\alpha \partial_x p\).

For the ionic contribution to the term \(J_i \nabla H_i\) consider the gradient of Eq. \((A6)\). First, the term \(\bar{J}_i \partial_x T\) vanishes in equilibrium. Meanwhile, Eq. \((A5)\) also contains a term proportional to the thermal expansivity of the solvent \(\partial T \ln V\), the gradient of which vanishes in the bulk. In equilibrium \(\partial_t H_i = 0\) because the solvent chemical potential is uniform throughout the cell. All these terms vanishing in equilibrium implies that \(J_i \partial_x H_i\) is proportional to \(J_i^2\) (or higher powers in \(J_i\)) and therefore vanishes faster than reversible contributions that go as \(\dot{\alpha}_{irr} \sim I\). We conclude that \(J_i \partial_x H_i\) does not contribute to reversible heating. Moreover, we see that the ratio \((J_+ + J_-) \nabla k_BT/\dot{\alpha}_{irr}\) also goes to zero since for the system of interest both the neutral salt current \((J_+ + J_-)\) and temperature variations \(\nabla T\) are very small. We therefore omit \(J_i \nabla H_i\) from Eq. \((B6)\) that now simplifies to the heat equation Eq. \((B0)\)

\[
\varrho c_p \partial_t T = \kappa \partial_x^2 T + \dot{\alpha}_{irr} + \dot{\alpha}_{rev}.
\]

Note that our derivation of this equation differs from the one presented in [14]. These authors started from internal energy balance (similar to our Eq. \((B3)\)) but lacking the term \(IE\), with this term appearing in the heat equation via the partial molecular enthalphy that they claim to be \(\bar{H}_i = \bar{\mu}_i - T (\partial \mu_i/\partial T)\).

Appendix C: Excess correlations

Electrolytic partial molar enthalphy Eq. \((A5)\) is welldocumented in the chemistry literature [14, 15] for the electro-neutral bulk. Instead of the term proportional to the thermal expansivity of the solvent, discussed at length above, usually excess chemical potential due to
ionic correlations are considered, via Debye-Hückel (DH) theory where \( \beta \mu^{\text{exc}}(T, \rho_s) = -\lambda_\mu/2\lambda_D \), or extensions thereof that include for instance finite ion size. In the bulk, adding \( \mu^{\text{exc}} \) will not contribute to the reversible heating since both \( \partial T, \rho_s \) and \( \partial T, \rho_s \) vanish in equilibrium. Meanwhile, the assumptions underlying DH theory are strongly violated in the EDL where same-sign counterions are at high density. We therefore expect the DH heating rates of [14], with a significant non-zero contribution in the EDL (see Fig. (6) of [14]), to be unreliable. This is substantiated by our Fig. 2(a) which shows that the solutions to the PNPh model as formulated in this Letter for slow charging coincide with the adiabatic temperature rise as predicted by the thermodynamic identity Eq. (2). Had we added ionic correlations via the formulation of [14], that is, only in the partial molecular enthalpy to only affect the PNPh equations, we would have found only the black dotted lines of Fig. 2(a) shifted, but not red line of the thermodynamic results of Eq. (2). If first-principles modeling is desired, excess ion correlations should be incorporated at the level of the grand potential functional Eq. (6), to impact (via the electrochemical potential) both the EDL and the bulk, in as well as out of equilibrium.

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