

Toward a Drift-Diffusion Device Conceptualization of Alkali-Ion Rocking-Chair Batteries

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Though rocking-chair batteries are ubiquitously associated with driving electronic devices, descriptions of their dynamical operation have generally been decoupled from the conventional drift-diffusion framework applied to solid-state electronic devices—the latter having enjoyed enormous success in the design of ubiquitous technologies including transistors, solid-state lasers, and light-emitting diodes. Building on long-standing Newman-type descriptions of battery operation, herein we discuss and present a theoretical framework for also conceptualizing the operation of alkali-ion rocking-chair batteries in terms of a competition between ion drift and diffusion via forces and concentration gradients, respectively. It is argued that the key link needed to facilitate a stronger physical bridge between coupled ionic and electronic degrees of freedom lies in the concept of a quasielectric field acting on ions between heterojunctions of ionic materials; a concept borrowed from the solid-state-device literature, where it has been extensively applied in heterojunction devices for decades, and extended in this work via the internal-energy contribution per ion particle. Within a model polymer redox battery system, for which a zero-vacuum reference energy for ions is also proposed, this approach is shown to capture standard battery concepts, including charging, discharging, capacity loss, internal resistances, nonequilibrium charge densities, and operating voltages. In this manner, the findings presented seek to provide a fundamental lasting bridge between electrochemical and electronic device descriptions.

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I. INTRODUCTION

The study of devices that couple ionic and electronic properties in an electrochemical context has expanded enormously in the past decade or so [1–6]. This, in turn, has stimulated increasing investigation into their operational properties within the solid-state physics community [7–10]. All of this exploration, at its heart, has been nucleated by the enormous technological success of alkali-ion rocking-chair batteries [11,12]. Thus, arguably, the most prominent focus for the further integration of solid-state and electrochemical-device descriptions has been in the exploration of such batteries [7,8,13,14]. The essence of their operation consists of the free motion of ions across a double junction comprised of an anode, a

separator-electrolyte, and a cathode, as shown in Fig. 1. During discharging, the ions diffuse across the separator-electrolyte from the anode to the cathode [see Fig. 1(a)], while under charging the opposite occurs through the action of a power source [see Fig. 1(b)]. In both cases, electron flow occurs through the external circuit, since their internal flow across the separator-electrolyte is prevented by its electrically insulating nature [15]. The term “rocking-chair” arises from the manner in which ions are “rocked” back and forth from the anode to the cathode across repeated discharging and charging cycles (again see Fig. 1) [11,12].

In virtually all mesoscopic to macroscopic sized solid-state devices, including electronic and optoelectronic variations, the drift-diffusion formalism is ultimately employed to physically understand and interpret operational properties within a system of governing continuity equations [16–19]. Drift refers to the action of force on carriers, such as internal fields, while diffusion refers to carrier motion from higher- to lower-concentration regions (e.g., entropic contributions in the dilute limit [17]). This includes material heterojunctions wherein the conceptualization

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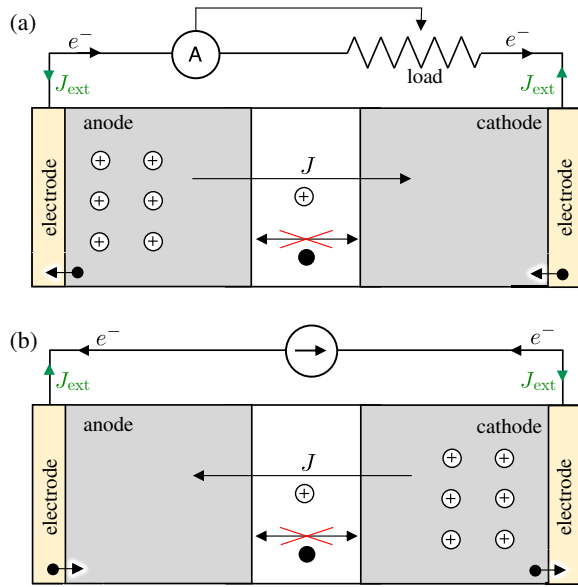


FIG. 1. The general alkali-ion rocking-chair battery operation with ions (open positive circles) moving from the anode and cathode during charging and discharging, while electrons (filled black circles) move between the anode and cathode through an external circuit. (a) Constant-current discharging accomplished by dynamically varying the load resistance via feedback from an ammeter. (b) Charging through the application of a constant-current source that drives electrons from the cathode to the anode. In each case, at the electrode-anode and cathode-electrode interfaces, the current inside the battery (J) equals the current in the external circuit (J_{ext}). Positive current flow is from left to right inside the battery.

and tailoring of quasielectric fields has led to enormous advances in operational functionality [20]. From a solid-state perspective, a rocking-chair battery can be viewed schematically as a double-heterojunction electrical device with an additional electrochemical degree of ionic freedom across its heterojunctions (see Fig. 1) [7,8,13,21]. This then leads to the question of how one might view the additional, though crucial, degree of ionic freedom within a similar drift-diffusion framework. Indeed, such a link would form a crucial fundamental bridge between the device physics and the electrochemistry literature.

A significant body of work exists on capturing the operation of rocking-chair batteries via a system of continuum equations describing current flow from a chemical perspective [22–24]. This includes the seminal Newman-type models of Li-ion batteries and expansions upon it [25–27]. Moreover, a wide range of work has been done to map the solid-state electronic structure properties of such batteries toward operational properties such as the open-circuit voltage [7,8,14,28,29]. Yet, despite these important contributions, very little has been done to map these approaches to the drift and diffusion conceptualization common in the solid-state-device literature. This can be argued to be due

to the relatively slow emergence of electrochemical investigations in the physics literature [6,8,14,28–35]. In this work, we seek to facilitate a theoretical approach whereby the ionic and electronic degrees of freedom in a rocking-chair battery can both be understood in the context of drift and diffusion. This is shown to emerge from a conceptualization of ion flow strongly impacted upon by quasielectric fields, that in turn arise from internal-energy variations per ion particle. Moreover, by further bridging electronic and ionic formulations of the vacuum reference energy in device descriptions, we seek to foster the emergence of a perspective whereby ionic and electronic degrees of freedom are formulated within analogous solid-state concepts; i.e., a framework through which the basic functionality of rocking-chair batteries can be intuitively grasped from a device perspective.

To this end, our study is divided into four additional sections. First, in Sec. II, the general theoretical framework is expanded upon in depth, with a particular emphasis on the conceptualization of quasielectric fields. Following this, a model redox polymer battery system is outlined to demonstrate the utility of the proposed approach (Sec. III). For this system, the analytical electrochemical potential and voltage expressions are readily provided. Next, general results concerning drift-diffusion properties under equilibrium, charging, and discharging properties are provided by solving the underlying continuity equations (Sec. IV). Emphasis is placed upon solving the fundamental governing equations for electrons and ions, so as to enable direct analysis of drift and diffusion properties—rather than higher-order multiscale complexities [36]. Lastly, brief summary conclusions are provided, with an outlook for possible future work (Sec. V).

II. THEORETICAL APPROACH

A. Battery-voltage conceptualizations

For an alkali ($\mathcal{A}$) ion battery, with only one electron lost or gained per ion, the battery voltage (V_B) is often defined in terms of the difference between the anode (denoted by subscript a) and cathode (denoted by subscript c) chemical potentials:

$$[V_B]_{\text{std}} = (\mu_{\mathcal{A}|a} - \mu_{\mathcal{A}|c})/q \quad (1)$$

$$= ((\mu_{\mathcal{A}^+|a} + \mu_{e^-|a}) - (\mu_{\mathcal{A}^+|c} + \mu_{e^-|c}))/q \quad (2)$$

$$= (\Delta\mu_{e^-} + \Delta\mu_{\mathcal{A}^+})/q, \quad (3)$$

$$\Delta\mu_{e^-} = \mu_{e^-|a} - \mu_{e^-|c}, \quad (4)$$

$$\Delta\mu_{\mathcal{A}^+} = \mu_{\mathcal{A}^+|a} - \mu_{\mathcal{A}^+|c}. \quad (5)$$

For the purposes of this study, the above is referred to as the standard (std) voltage expression for rocking-chair alkali batteries [32,37,38]—the elementary charge is denoted by q . All chemical potentials (μ) in Eqs. (1)–(5)

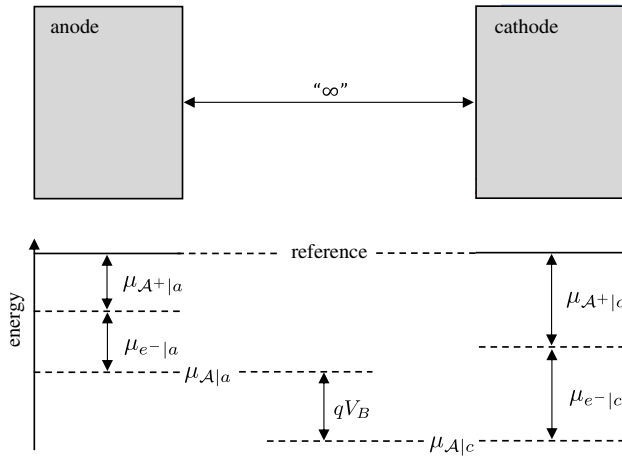


FIG. 2. The standard approach for determining the voltage (V_B) of an alkali-ion (A^+) “rocking-chair” battery by considering the chemical potentials (μ) of the anode and cathode in isolation (e.g., at an “infinite” distance). All chemical potentials are determined with respect to a defined reference.

refer to the anode- and cathode-material systems in isolation, prior to any exchange of species (electrons or ions), as shown in Fig. 2. *Herein, chemical potentials are defined in joules per particle.* Electron quantities are denoted by a subscript e^- , while alkali-ion quantities are denoted by subscript A^+ .

Upon achieving contact, via an intermediate separating medium as illustrated in Fig. 3(a), the anode and cathode can exchange ions but not electrons. As practically required for such batteries, it is assumed that the separator region is a near-perfect insulator with respect to electron flow [15,21,37]. Consequently, to realize a constant ion-equilibrated (ion-eq) electrochemical potential, an electrostatic potential (ϕ) develops across the junction along the spatial direction x , through the exchange of ions as shown in Fig. 3(b). This condition can be formally expressed as

$$[\bar{\mu}_{A^+|a} - \bar{\mu}_{A^+|c}]_{\text{ion-eq}} = 0, \quad (6)$$

$$\bar{\mu}_{A^+|a}(x) = \mu_{A^+|a} + q\phi(x), \quad (7)$$

$$\bar{\mu}_{A^+|c}(x) = \mu_{A^+|c} + q\phi(x), \quad (8)$$

in the absence of current flow (J ; see Fig. 1) between the anode and cathode. In this manner, under ion-equilibrium conditions, any displacement between $\mu_{A^+|a}$ and $\mu_{A^+|c}$ in the isolated materials (see Fig. 2) is resolved by the corresponding electrochemical potential forms in Eqs. (7) and (8). All electrochemical potentials are denoted by placing an overbar above a given chemical potential [39] (e.g., $\bar{\mu}$). The term ion equilibrium (or ionic equilibrium) is intended to emphasize that the electrochemical potentials of the alkali ions have equilibrated but not that of electrons.

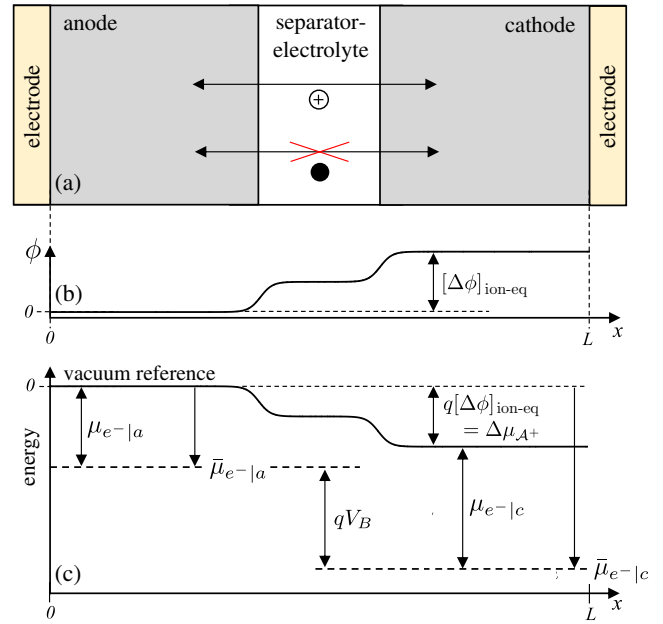


FIG. 3. (a) An anode and cathode in contact through a separator-electrolyte, which allows ionic flow (open positive circle) but blocks electron flow (solid filled circle). (b) Ion equilibration leads to the formation of an electrostatic potential ϕ across the spatial position x , extending through the junction (middle schematic figure). (c) From the perspective of electrons, the overall electrochemical potential (qV_B) shift includes both the difference in electron chemical potentials from each side and the electrostatic potential shift introduced by ion electrochemical equilibration across the junction.

Hence, it is not a global equilibrium. If it were, then energy storage would not be possible.

When the anode and cathode are in ionic contact [see Fig. 3(a)], the battery voltage can generally be expressed as

$$V_B = (\Delta\bar{\mu}_{e^-} + \Delta\bar{\mu}_{A^+})/q, \quad (9)$$

$$\Delta\bar{\mu}_{e^-} = [\bar{\mu}_{e^-|a}]_{x=0} - [\bar{\mu}_{e^-|c}]_{x=L}, \quad (10)$$

$$\Delta\bar{\mu}_{A^+} = [\bar{\mu}_{A^+|a}]_{x=0} - [\bar{\mu}_{A^+|c}]_{x=L}, \quad (11)$$

$$\bar{\mu}_{e^-|a}(x) = \mu_{e^-|a} - q\phi(x), \quad (12)$$

$$\bar{\mu}_{e^-|c}(x) = \mu_{e^-|c} - q\phi(x), \quad (13)$$

such that it is given by the difference between the electrochemical potentials at the external electrode contact points to the anode and cathode; these points are defined at $x = 0$ and $x = L$, respectively, in Fig. 3(b). Note that electrons (e^-) see the formed potential (ϕ) oppositely to the positive ions (A^+); hence the sign change between Eqs. (7) and (8) and Eqs. (12) and (13). Although under ionic equilibrium it is necessary for the electrochemical potentials to be at least internally equilibrated (flat) within the anode and cathode, as shown in Fig. 3(c), it is still useful to pick a specific point for defining their difference (i.e., 0 and L) for charging and discharging conditions. Now, when the ions

are in equilibrium, the general voltage expression in Eqs. (9)–(13) takes the specific form

$$\begin{aligned} [V_B]_{\text{ion-eq}} &= [\Delta\bar{\mu}_{e^-} + \Delta\bar{\mu}_{\mathcal{A}^+}]_{\text{ion-eq}}/q \\ &= [\mu_{e^-|a} - \mu_{e^-|c}]/q - [\phi(0) - \phi(L)]_{\text{ion-eq}}, \end{aligned} \quad (14)$$

since this state requires $\Delta\bar{\mu}_{\mathcal{A}^+} = 0$ per Eqs. (6) and (11). Further equating the standard voltage expression in Eq. (2) with that in Eq. (14), one obtains

$$\begin{aligned} [\Delta\phi]_{\text{ion-eq}} &= [\phi(L) - \phi(0)]_{\text{ion-eq}} \\ &= (\mu_{\mathcal{A}^+|a} - \mu_{\mathcal{A}^+|c})/q = \Delta\mu_{\mathcal{A}^+}/q, \end{aligned} \quad (15)$$

meaning that the alkali-ion chemical potential difference ($\Delta\mu_{\mathcal{A}^+}$) between the separate anode and cathode materials is manifest as an internal electrostatic potential difference across the anode-separator-cathode junction [compare Fig. 2 with Figs. 3(a) and 3(b)]. Electrons “see” the chemical potential difference between the alkali species in the anode and cathode as a further electromotive impetus, in addition to their own intrinsic chemical potential difference [$\Delta\mu_{e^-}$ in Eq. (4)] [8,14,37,40]. In this manner, the combined chemical potential difference in Eq. (1) is manifest as an overall electron electrochemical potential difference in Eq. (14) that drives electron flow from the anode to the cathode via an external circuit. Stated otherwise, upon contact between the anode and cathode materials [as per Fig. 3(a) via a separator-electrolyte], electrons traversing from one electrode to another through an external circuit see not only their own chemical potential difference ($\Delta\mu_{e^-}$, commonly referred to as their Fermi-level offset in solid-state anodes and cathodes [37]), but also the additional electromotive impetus ($[\Delta\phi]_{\text{ion-eq}}$) created by ions attempting to reach electrochemical equilibrium via the separator-electrolyte region [this is shown in Figs. 3(b) and 3(c)]. This conclusion reinforces the idea that what electrons “see” as an electromotive force is shaped not only by their own chemical potential difference but also by the potential induced through ion redistribution. It aligns with the Kroemer-inspired quasidelectric field framework [20]: a potential profile emerging not only from an externally applied voltage but also from internal material energy changes that produce the same effect—a subject we shall expand upon shortly.

A number of questions emerge from this line of argumentation [8,13,14]. First, how are the alkali ions driven to reach this ionic equilibrium? Second, what is the distribution of the potential drop $\phi(x)$ created by ions attempting to equilibrate? Third, what is the nature of ion flow and charge displacement when achieving ionic equilibrium? Fourth, how does ion flow interact with electron flow during discharging and charging? Fifth, how is the electrostatic potential across the battery junction modified by

such charging and discharging conditions (i.e., when not in ionic equilibrium)? The final four points of inquiry have fundamental origins in the continuity equations for electrons and ions, as will be outlined in Sec. II C [22–24]. The first point of inquiry is discussed next, in Sec. II B.

B. The quasidelectric field for alkali-ion species

To enable a more general discussion beyond the junction in Fig. 3, consider two distinct alkali-ion ($\mathcal{A}^+$) hosts α and β into which ions may be inserted or removed without altering their ionic charge state (e.g., +1 to neutral). Within both isolated materials (or media), one can express their respective chemical potentials via

$$\mu_{\mathcal{A}^+|\alpha} = \left[\frac{\partial(U_\alpha + PV - S_\alpha T)}{\partial N_{\mathcal{A}^+}} \right]_{T,P,N_{\mathcal{A}^+} \neq N_o}, \quad (16)$$

$$\mu_{\mathcal{A}^+|\beta} = \left[\frac{\partial(U_\beta + PV - S_\beta T)}{\partial N_{\mathcal{A}^+}} \right]_{T,P,N_{\mathcal{A}^+} \neq N_o}, \quad (17)$$

where the number of alkali species $N_{\mathcal{A}^+}$ varies while holding all other species N_o (including electrons) fixed. Between any two materials, we shall focus only on the variations of entropy (S_α or S_β) and internal energy (U_α or U_β) with respect to the particle number—the host is indicated by a subscript. Let us further assume that the temperature (T) and pressure (P) are not only constant within a material or medium but also upon an ion ($\mathcal{A}^+$) exchange between α and β . Finally, leaving the impact of the entropy changes between any two regions for later discussion [37], and treating volume (V) changes as negligible to simplify the discussion [41], we first focus on the internal-energy contributions to the chemical potentials [in Eqs. (16) and (17)], expressed as

$$\varepsilon_{\mathcal{A}^+|\alpha} = \left[\frac{\partial U_\alpha}{\partial N_{\mathcal{A}^+}} \right]_{T,P,N_{\mathcal{A}^+} \neq N_o}, \quad (18)$$

$$\varepsilon_{\mathcal{A}^+|\beta} = \left[\frac{\partial U_\beta}{\partial N_{\mathcal{A}^+}} \right]_{T,P,N_{\mathcal{A}^+} \neq N_o}. \quad (19)$$

The internal-energy change is taken with respect to some reference where a given $\mathcal{A}^+$ species is placed upon removal from its host material or medium. Let us assume that the zero reference energy for the $\mathcal{A}^+$ ion consists of its removal from the solid far away to the vacuum, as shown in Fig. 4(a). Although similar to the concept of a vacuum reference for electrons per Fig. 3(c) [16,17], in the case of an ion there is work done on both the ion and the host media or materials (α and β) during addition and removal [42]. Hence both forms of work contribute to the internal-energy

change in Eqs. (18)–(20) when an ion is moved far away to or from the proposed vacuum reference in Fig. 4(a). Moreover, this internal-energy change will more likely reflect the mean internal-energy change amongst the many possible coordinate configurations of an ion in its host media or material. This will be discussed later in the context of solvated ions (see Sec. III). Here, it can be seen that through the choice of such a reference, one can then quantify the offset in the internal-energy change,

$$\Delta\epsilon_{\mathcal{A}^+} = \epsilon_{\mathcal{A}^+|\alpha} - \epsilon_{\mathcal{A}^+|\beta}, \quad (20)$$

when picking up an ion from β and placing it in α . Importantly, $\epsilon_{\mathcal{A}^+|\alpha}$ and $\epsilon_{\mathcal{A}^+|\beta}$ are both negative energies (below the zero-vacuum reference for ions). This is analogous to the vacuum reference convention applied in the electronic device literature [16,17,43], where the conceptual equivalence to $\epsilon_{\mathcal{A}^+}$ is the ionization potential energy cost when removing an electron from the conduction-band minimum. Thus, $\epsilon_{\mathcal{A}^+|\alpha}$ (or $\epsilon_{\mathcal{A}^+|\beta}$) is the internal-energy cost of an alkali-ion removal to its vacuum reference.

Now, instead of examining the removal of an ion to the vacuum reference from one material and subsequent placement again from the vacuum into another material [Fig. 4(a)], consider next the formation of a junction between α and β where the composition varies continuously (via a stoichiometric parameter $0 \leq \kappa \leq 1$) in the form of $\alpha_{1-\kappa}\beta_\kappa$, as shown in Fig. 4(b). In principle, the width of this junction (W) may even be as small as one atomic monolayer (reflecting an abrupt interface), but in practice it often occurs over a much longer diffuse interface [7,9,19,20]. Furthermore, in Fig. 4(b) the vacuum reference alignment is initially held flat so as to reflect that neither electrons (e^-) nor alkali ions ($\mathcal{A}^+$) have yet moved in significant numbers across the junction. This means that in Fig. 4(b), only a single species (or a near-infinitesimal number) is moved per Eqs. (18)–(20) and the material compositions are precisely as indicated by the stoichiometric ratio κ . One can think of this configuration as the “instantaneously” formed junction prior to equilibration via the exchange of $\mathcal{A}^+$ or e^- . Under such conditions, since the material or medium composition is changing, so should a *continuous* grading occur in the internal energy. Specifically, from $\epsilon_{\mathcal{A}^+|\alpha}$ to $\epsilon_{\mathcal{A}^+|\beta}$, this internal-energy change follows a continuous form represented by $\epsilon_{\mathcal{A}^+}$ and illustrated schematically in Fig. 4(b).

Importantly, from the perspective of an alkali ion $\mathcal{A}^+$ moved continuously from α to β across this junction (without exiting to vacuum), the change in internal energy leads to a corresponding force on $\mathcal{A}^+$, given by

$$F_{\mathcal{A}^+} = -\frac{d\epsilon_{\mathcal{A}^+}}{dx} = +q\mathcal{E}_{\mathcal{A}^+} \quad (21)$$

and illustrated in Fig. 4(b). Note that we are only moving alkali ions ($\mathcal{A}^+$) and have kept all electrons (e^-) fixed

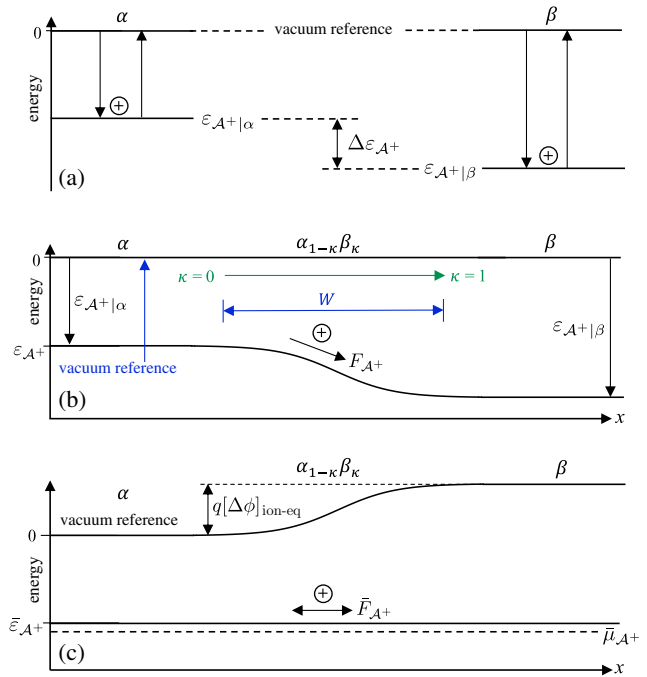


FIG. 4. (a) The internal-energy cost per $\mathcal{A}^+$ particle ($\epsilon_{\mathcal{A}^+}$) to remove an alkali ion (open positive circle) from two materials or media α and β to vacuum set as the reference at 0. (b) The vacuum alignment for an “instantaneous” junction alignment between materials α and β with a stoichiometry composition gradient $\alpha_{1-\kappa}\beta_\kappa$ across a width W . The internal energy per $\mathcal{A}^+$ particle ($\epsilon_{\mathcal{A}^+}$) varies continuously across this junction to provide a force of $F_{\mathcal{A}^+}$ on each $\mathcal{A}^+$ particle within the junction. (c) The ion equilibration of the junction after charge displacement with a flat alkali-ion electrochemical potential $\bar{\mu}_{\mathcal{A}^+}$. The electrointernal-energy cost per particle ($\bar{\epsilon}_{\mathcal{A}^+}$) includes the action of the electrostatic potential ϕ that is now present in the vacuum reference [see also Eq. (15) and Ref. [17]]. In reality, the charge-transfer (accumulation and depletion) contributions from ions will require some small variation in $\bar{\epsilon}_{\mathcal{A}^+}$ about the interface with respect to the flat equilibrated $\bar{\mu}_{\mathcal{A}^+}$. These variations are assumed to be very small and are not shown in the plot.

for the purposes of this discussion; also, entropic terms are excluded from this conceptualization of force [20]. This force $F_{\mathcal{A}^+}$, formed by the gradient in the internal energy per ion particle, drives the motion of ions from α to β . Following the convention used for electrons experiencing a variation in the ionization potential across heterojunctions, developed by Kroemer [20], one can further conceptualize the internal-energy action on ions in terms of a “quasielectric” field ($\mathcal{E}_{\mathcal{A}^+}$), as expressed in Eq. (21) [16,17]. It is a quasielectric field because it acts only on $\mathcal{A}^+$ ions and not on all other charges (e.g., e^-)—unlike a “true” electric field. This physical interpretation can be justified from first principles in terms of the underlying electrostatic forces acting on such an ion from the surrounding electrons and nuclei in the host medium or material—on which a detailed

discussion is provided in the Supplemental Material [44] (see also Refs. [42,45–48]).

Under action from such a quasielectric field, $\mathcal{A}^+$ ions seek to evolve toward a uniform electrochemical potential $\bar{\mu}_{\mathcal{A}^+}$, as shown in Fig. 4(c) and formerly discussed in the context of ionic equilibrium in Sec. II A. Yet, under such conditions, ionic equilibrium can only be accomplished by establishing a counter force (or flow) via a “true” electric field, defined by

$$\mathcal{E} = -\frac{d\phi}{dx}, \quad (22)$$

leading to the plot in Fig. 4(c), where the electrostatic potential (ϕ) is manifest in the curved profile of the vacuum potential [16,17,20]. The combined action of the internal energy per $\mathcal{A}^+$ particle ($\varepsilon_{\mathcal{A}^+}$) and the electrostatic potential leads to

$$\bar{\varepsilon}_{\mathcal{A}^+} = \varepsilon_{\mathcal{A}^+} + q\phi, \quad (23)$$

which can be termed the electrointernal energy per $\mathcal{A}^+$ particle. Moreover, the joint action of the charge displacement forming the electric field ($\mathcal{E}$) and quasielectric field ($\mathcal{E}_{\mathcal{A}^+}$) can be combined in an overall mean field acting on the ion with the form

$$\bar{\mathcal{E}}_{\mathcal{A}^+} = \mathcal{E}_{\mathcal{A}^+} + \mathcal{E} = -\frac{1}{q} \frac{d\bar{\varepsilon}_{\mathcal{A}^+}}{dx}. \quad (24)$$

In Eqs. (23) and (24), the additional incorporation of an overbar is employed in the same manner as an electrochemical potential so as to indicate the incorporation of electrostatic interactions originating from charge displacement or transfer [per Eqs. (7) and (8)]. Ultimately, the balance of ionic equilibrium is characterized by a flat electrochemical potential ($\bar{\mu}_{\mathcal{A}^+}$), as illustrated in Fig. 4(c). Notably, the chemical potential entropy contribution has been kept uniform throughout Fig. 4 by assuming $S_\alpha = S_\beta$ in Fig. 4(a). Generalizing further to entropy variations per Eqs. (16) and (17) brings us to the next point of the discussion.

C. Coupled Poisson continuity equations

Ultimately, for an ionic equilibrium to be reached there must be a flux of $\mathcal{A}^+$ species between two materials or media α and β , as shown in Fig. 4, or, furthermore, across an anode-separator-cathode junction as shown in Fig. 3. Moreover, any flow in charge correspondingly results in a current, which for alkali-ion species can be expressed in the form of drift and diffusion (diff) terms:

$$\begin{aligned} J_{\mathcal{A}^+} &= J_{\mathcal{A}^+|\text{drift}} + J_{\mathcal{A}^+|\text{diff}} \\ &= qu_{\mathcal{A}^+}\rho_{\mathcal{A}^+}\bar{\mathcal{E}}_{\mathcal{A}^+} - qD_{\mathcal{A}^+}\frac{\partial\rho_{\mathcal{A}^+}}{\partial x}. \end{aligned} \quad (25)$$

Here, the ion mobility ($u_{\mathcal{A}^+}$) and diffusion ($D_{\mathcal{A}^+}$) constants are assumed to be uniform throughout a battery system or junction to simplify the analysis. However, the governing equations can be readily modified to account for their nonuniformity [25–27]. All mobility (u) and diffusion terms (D) are coupled via the Einstein relation $u/q = D/k_B T$, where k_B is Boltzmann’s constant (with SI units employed). Importantly, as summarized earlier in Eq. (24), both the electric field and quasielectric field act within the drift term in Eq. (25). The displacement of the alkali-ion density ($\rho_{\mathcal{A}^+}$) is governed by the time (t) dependent continuity equation

$$\frac{\partial\rho_{\mathcal{A}^+}}{\partial t} = -\frac{1}{q}\frac{\partial J_{\mathcal{A}^+}}{\partial x}, \quad (26)$$

including under charging and discharging conditions. A similar current expression is arrived at for electrons, with the exception that electron flow occurs in the direction opposite to that of current flow, giving

$$\begin{aligned} J_{e^-} &= J_{e^-|\text{drift}} + J_{e^-|\text{diff}} \\ &= qu_{e^-}\rho_{e^-}\mathcal{E} + qD_{e^-}\frac{\partial\rho_{e^-}}{\partial x}. \end{aligned} \quad (27)$$

Time-dependent variation in the electron density (ρ_{e^-}) also follows a continuity equation:

$$\frac{\partial\rho_{e^-}}{\partial t} = +\frac{1}{q}\frac{\partial J_{e^-}}{\partial x}. \quad (28)$$

Importantly, the charge-displacement electric field ($\mathcal{E}$) is assumed to be the only drift-force contribution acting on electrons in Eq. (27). It acts on all charges and is arrived at via Eq. (22), with the potential (ϕ) further obtained from Poisson’s equation,

$$\epsilon\frac{\partial^2\phi}{\partial x^2} + \frac{\partial\epsilon}{\partial x}\frac{\partial\phi}{\partial x} = -q\rho, \quad (29)$$

$$\rho = \rho_{\mathcal{A}^+} - \rho_{e^-}, \quad (30)$$

and solved through Neumann boundary conditions by obeying the charge-neutrality condition

$$\int_0^L \rho_{\mathcal{A}^+}(x)dx = \int_0^L \rho_{e^-}(x)dx. \quad (31)$$

Herein, the dielectric constant (ϵ) is permitted to vary across material junctions (such as those depicted in Figs. 3 and 4). A quasielectric field term could also be introduced for electrons, and might be necessary for some systems [20,37], but is left out of this study so as to minimize complexity—for the same reason, convection terms

and diffusing separator-electrolyte anion species have also been excluded [25–27,49]. In either case, Eqs. (25)–(31) are coupled and must be solved together under all conditions. Finally, under active operation, during charging or discharging, the overall current flow within a battery (from 0 to L in Fig. 3) is a summation of current contributions from both ions and electrons:

$$J = J_{A^+} + J_{e^-} \quad (32)$$

Following the approach commonly applied in the device-physics literature, each of these current contributions can also be recast in terms of a nonequilibrium electrochemical potential [22–24].

III. MODEL SYSTEM

To further address the questions posed at the end of Sec. II A, it is necessary to select a model system for study. Many possible materials and media exist that may operate in the manner of a rocking-chair battery [8, 11, 12, 50]. However, to foster clarity it is preferable to begin by focusing on a model system whereby all the properties detailed in Sec. II can be estimated without resorting to first-principles calculations [37]. More elaborate calculations can be left to future work. Hence, the goal is to employ analytical expressions for chemical potentials so as to further cement the proposed framework in Sec. II, rather than to propose and/or analyze a state-of-the-art system at the edge of current performance metrics. To this end, the liquid media infused redox polymer system illustrated in Fig. 5(a) has been selected. If one assumes that the concentration of ions and redox species is sufficiently dilute (again, insights into performance limits are not the goal at this time [50]), then analytical expressions for the electrochemical potential quantities in Sec. II can be readily obtained. Crucially, this model system allows for alkali ion (A^+) motion throughout [as shown in Fig. 5(a)] but restricts electron motion to hopping only amongst redox groups in the anode and cathode. In this sense, it captures the ionic essence of rocking-chair batteries. Moreover, the use of a polymer to bind these redox groups avoids the further complication of capturing their flow via a further modified system of continuity equations, as discussed in Sec. II C [25–27]. A similar fixed-site approximation is made for the negative counter charges in the separator-electrolyte (denoted as $\rho_{e-|s}$ and opposite in sign to A^+ species). All of these points are discussed in depth below.

A. Alkali-ion electrochemical potential

If the alkali-ion concentration is sufficiently dilute, so that ion-ion interactions can be largely ignored [37], then to first order the internal energy per ion expressed by Eqs. (18)–(20) can be approximated analytically through the

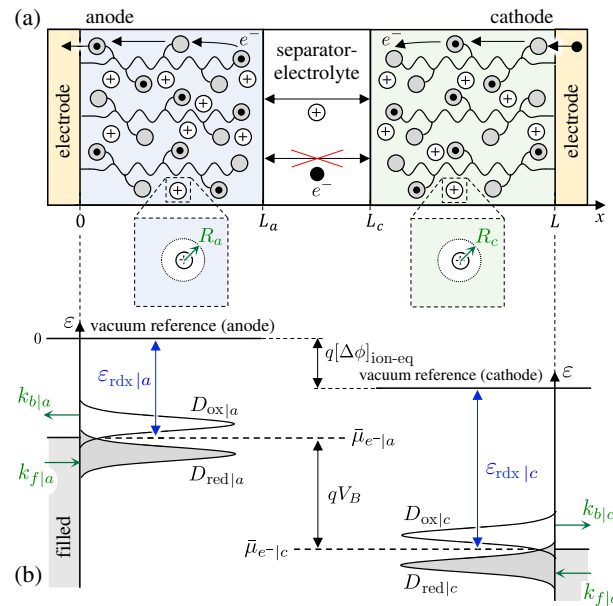


FIG. 5. The model system employed in this study. (a) The anode and cathode consist of a redox polymer infused with liquid media able to solvate alkali cations (indicated by positive circles). Oxidized redox groups are indicated by gray circles, while those that are reduced contain a further solid filled circle representing an added electron. A half-discharged configuration is shown, with electrons (filled black circles) exiting the anode and reaching the cathode. Electrons (e^-) diffuse by hopping between polymer redox groups [50]. Cations diffuse throughout and can cross the separator-electrolyte. Electrons (e^-) are restricted to motion only in the anode (blue) and cathode (green) regions and undergo transfer with the metal electrodes (light orange). The diffusing alkali ions in the anode (blue) and cathode (green) liquid media are characterized by solvation radii (R_a and R_c , respectively), as shown in the lower enlarged insets. (b) The Gerischer-Hopfield energy-level diagram for the oxidized and reduced states (D_{ox} and D_{red} , respectively), with distinct distributions for the anode (a subscript) and cathode (c subscript) redox polymers separated by the bias voltage $qV_B = \bar{\mu}_{e^-|a} - \bar{\mu}_{e^-|c}$. The electrode-reactant electron transfer to oxidized states (k_f) and from reduced states (k_b) are indicated in green. Filled electron states in the electrodes are shaded gray, while empty electrode states are unshaded. They are separated by the electrode electrochemical potential (solid line), which is aligned (or equivalent to) the respective quantity in the anode and cathode. At the assumed half-charged (or half-discharged) configuration, the reference internal-energy cost of removing an electron in each region ($\varepsilon_{\text{rdx}|a}$ and $\varepsilon_{\text{rdx}|c}$ in blue) aligns with the electron chemical potentials in each region ($\mu_{e^-|a}$ and $\mu_{e^-|c}$)—which is not the case at all charge states.

Born solvation model, to give

$$\varepsilon_{\mathcal{A}^+|a} \approx -\frac{Z_{ion}^2 q^2}{8\pi\epsilon_0 R_a} \left(1 - \frac{1}{\epsilon_a}\right), \quad (33)$$

$$\varepsilon_{\mathcal{A}^+|c} \approx -\frac{Z_{ion}^2 q^2}{8\pi\epsilon_0 R_c} \left(1 - \frac{1}{\epsilon_c}\right), \quad (34)$$

for the anode and cathode regions, respectively [30,50–53]. Moreover, for alkali ions $Z_{ion}=+1$. The ion-solvation radii (R_a and R_c) and dielectric constants (ϵ_a and ϵ_c) between the anode (subscript a) and cathode (subscript c) can be altered by simply changing the solvating liquid media in each region— ϵ_0 is the permittivity of free space.

Crucially, Born solvation energies are directly arrived at with respect to the placement of an ion in the vacuum (in isolation) far away from the host solvation media and thus represent a direct physical analog of the internal-energy change per ion discussed in the context of Fig. 4(a). The expressions in Eq. (33)–(34) are a summation of electrostatic energy-lowering action of the polarized solvent on the ion and the opposing work done by the ion on the solvent molecules when polarizing the surrounding media (a detailed discussion is provided in Ref. [51] and citations therein). Importantly, this same competition between action of the host media or material on the ion and corresponding action of the ion on the surrounding media or material exists for all systems and leads to the general form given by Eqs. (18)–(20). It is only the interactions between ions and the surrounding media that changes from system to system [37], many of which would require first-principles methods to estimate [8,37]. Thus, the internal-energy change per ion referenced to vacuum [as summarized in Fig. 4(a)] can be argued to be a general property so long as the ionic charge state ($\mathcal{A}^+$) is preserved during such a transition. Moreover, in the case of solvation there are many possible coordinate configurations from which an ion can be removed and thus $\epsilon_{\mathcal{A}^+}$ is better viewed as a mean energy for ion addition and removal [51,52]. The more general treatment of this averaging assumption, and possible exceptions to it in the solid state, are left to future work—further discussion is given in the Supplemental Material [44] (see also Ref. [42]).

Now, if we assume that $R_a \geq R_c$ and $\epsilon_a < \epsilon_c$, then one obtains $\epsilon_{\mathcal{A}^+|a} > \epsilon_{\mathcal{A}^+|c}$, as illustrated in Fig. 4(a). There are several selections of solvation media that could satisfy this requirement [54]. However, the further necessity of a separator-electrolyte [see Figs. 3(a) and 5(a)] implies that such a region should have an internal-energy interaction bounded by $\epsilon_{\mathcal{A}^+|a} > \epsilon_{\mathcal{A}^+|s} > \epsilon_{\mathcal{A}^+|c}$. Note again that all internal-energy changes per ion are negative relative to vacuum. Subscript s denotes the separator-electrolyte region. This arrangement would lead to the ionic equilibrium electrostatic profile in Fig. 3(b) via the successive formation of two junctions in the manner illustrated in Fig. 4.

We do not speculate on the precise nature of the separator-electrolyte in Fig. 5(a). However, it might plausibly function similarly to the recently reported sulfonated spirobifluorene-based polymer [55]. This enables one to treat the negatively charged species of the separator-electrolyte as a fixed negative group [e.g., SO_3^- as an

immobile separator-electrolyte negative charge density ($\rho_{e-|s}$) density in Eqs. (25)–(32)] and thereby avoid the further complexity of modeling diffusing anion species within the electrolyte per the adopted continuity-equation expressions in Sec. II C [54]. Regardless, negative species and/or groups are necessary as a balancing counter charge to alkali ions ($\mathcal{A}^+$) in the separator region, just as they are in the anode and cathode—otherwise, unsustainable electric fields would build up and operation would not be possible.

To arrive at an electrochemical potential expression for ions per Fig. 2, the assumption of a reasonably dilute ion concentration further enables an ideal-gas approximation [37,56] entropy term in Eqs. (16) and (17), yielding

$$\begin{aligned}\bar{\mu}_{\mathcal{A}^+}(x) &= \bar{\epsilon}_{\mathcal{A}^+}(x) + k_B T \ln(\rho_{\mathcal{A}^+}(x)/\rho_o) \\ &= \epsilon_{\mathcal{A}^+}(x) + q\phi(x) + k_B T \ln(\rho_{\mathcal{A}^+}(x)/\rho_o) \\ &= \mu_{\mathcal{A}^+}(x) + q\phi(x),\end{aligned}\quad (35)$$

which extends across the entire anode-separator-cathode junction, as shown in Figs. 3 and 4. Here, ρ_o is the reference concentration at which $\epsilon_{\mathcal{A}^+}$ is measured. Notably, $\epsilon_{\mathcal{A}^+}$ has been shown to converge asymptotically at moderately dilute concentrations [52]. The same reference value of ρ_o is applied in all regions per Figs. 3, 4, and 5.

B. Electron electrochemical potential

Given the fixed number of redox sites available to store electrons, the entropy term in both the anode and cathode can be approximated by a lattice-gas model [37,56] in the form of

$$k_B T \ln\left(\frac{\gamma}{1-\gamma}\right), \quad (36)$$

where $\rho_{\text{red}} = \gamma\rho_{\text{max}}$ is the fraction of reduced sites amongst the total redox site density of ρ_{max} and, correspondingly, the density of oxidized states is given by $\rho_{\text{ox}} = (1-\gamma)\rho_{\text{max}}$ —hence $0 \leq \gamma \leq 1$.

For a given occupation fraction (γ), the overall chemical potential at the anode or cathode can be obtained by focusing on its equilibration alignment with the given metal electrode. To this end, the Gerischer-Hopfield formalism [30,34,57–60] expresses the internal-energy cost of adding or removing an electron from a redox site as

$$D_{\text{red}}(\epsilon) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\epsilon - \epsilon_{\text{rdx}} + \lambda)^2}{4\lambda k_B T}\right), \quad (37)$$

$$D_{\text{ox}}(\epsilon) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\epsilon - \epsilon_{\text{rdx}} - \lambda)^2}{4\lambda k_B T}\right). \quad (38)$$

Here, D_{ox} and D_{red} , respectively, describe the probability of finding a reduced and oxidized state at a given

single-particle energy ε below vacuum [34]. This is governed by the heterogenous reorganization energy (λ), with each respective distribution center offset by $\pm\lambda$ from the midpoint energy ε_{rdx} as shown in Fig. 5(b). The precise location of these Gerischer-Hopfield distributions would ideally vary through the selection of distinct redox groups in the anode (a subscript appended) and cathode (c subscript appended) so as to further the electronic contributions to the overall voltage V_B such that $\varepsilon_{\text{rdx}|c} < \varepsilon_{\text{rdx}|a}$ per Fig. 5(b). The reorganization energies of the anode (λ_a) and cathode (λ_c) may also differ for such systems. With respect to the discussion in Sec. IIC, it is also important to note that the Gerischer-Hopfield formalism can also be applied to arrive at an electron diffusion constant ($\mathcal{D}_{e^-}$) between redox groups as discussed in Refs. [61] and [62].

At any charged or discharged configuration during ionic equilibrium when $J = 0$ per Eq. (32), conditions at each electrode requires that the time-averaged forward (k_f) and backward (k_b) electron transfer to or from the redox groups (from or to the electrodes) are in balance such that

$$[k_f \rho_{\text{ox}}]_{\text{ion-eq}} = [k_b \rho_{\text{red}}]_{\text{ion-eq}}, \quad (39)$$

assuming that the surface-averaging integral for electron transfer works out to the same value on each side of Eq. (39) [34,63]. For any given metal-electrode contact, by integrating through Eqs. (37) and (38) with respect to a Fermi distribution, these rates take on the approximate ratio relation [30]

$$\frac{k_f}{k_b} \approx \frac{\exp\left(\frac{-(\lambda - 2(\mu_{e^-} - \varepsilon_{\text{rdx}}))}{4k_B T}\right)}{\exp\left(\frac{-(\lambda + 2(\mu_{e^-} - \varepsilon_{\text{rdx}}))}{4k_B T}\right)}, \quad (40)$$

with further details given in the Supplemental Material [44] (see also Refs. [30,34]). Note that the screening potentials at the electrode-anode and cathode-electrode interfaces are not modeled in this study and are instead assumed to form on a much faster timescale than charging or discharging [34,64,65]. Applying the condition expressed by Eq. (39) via Eq. (40) results in the electron chemical potential given by

$$\mu_{e^-} = \varepsilon_{\text{rdx}} + k_B T \ln\left(\frac{\gamma}{1 - \gamma}\right) \quad (41)$$

for a given electrode under ionic equilibrium. The expected lattice-gas entropy term provided in Eq. (36) is retained [37,56], where $\mu_{e^-} = \varepsilon_{\text{rdx}}$ persists only at the reference concentration, when there is an equal number of oxidized and reduced states ($\gamma = 0.5$), as depicted in Fig. 5(b). Note that μ_{e^-} and ε_{rdx} are measured with respect to the electronic vacuum level of each material (e.g., anode and cathode), whereas the electrochemical potential $\bar{\mu}_{e^-}$ and its corresponding internal-energy term $\bar{\varepsilon}_{\text{rdx}}$ are measured with

respect to the leftmost electrode vacuum potential for the entire device in Fig. 5 [16,17]. This is needed to account for the role of the electrostatic potential ϕ in the separation of electrochemical potentials as discussed in Sec. IIA. Hence, expanding out Eqs. (12) and (13) with respect to Eq. 41, one obtains

$$\begin{aligned} \bar{\mu}_{e^-|a} &= \varepsilon_{\text{rdx}|a} - q\phi(x) + k_B T \ln\left(\frac{\gamma_a(x)}{1 - \gamma_a(x)}\right) \\ &= \bar{\varepsilon}_{\text{rdx}|a} + k_B T \ln\left(\frac{\gamma_a(x)}{1 - \gamma_a(x)}\right), \end{aligned} \quad (42)$$

$$\begin{aligned} \bar{\mu}_{e^-|c} &= \varepsilon_{\text{rdx}|c} - q\phi(x) + k_B T \ln\left(\frac{\gamma_c(x)}{1 - \gamma_c(x)}\right) \\ &= \bar{\varepsilon}_{\text{rdx}|c} + k_B T \ln\left(\frac{\gamma_c(x)}{1 - \gamma_c(x)}\right) \end{aligned} \quad (43)$$

for both the anode and cathode per Figs. 3(c) and 5(b), with distinct reduced site fractions γ_a and γ_c provided for the anode and cathode, respectively. These fractions may adopt a spatial dependence (x) across the entire device (see Figs. 3 and 5).

Interestingly, a comparison between Eqs. (42) and (43) and Eqs. (9)–(13) demonstrates that a battery voltage can still be arrived at in this model system when $[\Delta\phi]_{\text{ion-eq}} = 0$ so long as $\varepsilon_{\text{rdx}|c} < \varepsilon_{\text{rdx}|a}$. Such a situation could be reached by maintaining the same liquid media in the anode (blue) and cathode (green) in Fig. 5(a) such that $\varepsilon_{A^+|a} = \varepsilon_{A^+|c}$ per Eqs. (33) and (34), while assigning suitably designed distinct redox groups on each side. Thus, the analytical separation of electronic and ionic electrochemical potential expressions enabled by this model system (Fig. 5) demonstrates that it is possible to have a system in which the battery voltage is almost entirely determined by a difference in electron chemical potentials (Fermi levels) between the anode and cathode, as has been occasionally put forward in the literature [14,66,67]. However, this is more likely to be an exception than the case in general. It could only occur when the internal energy per alkali ions is the same (or nearly so) in both the anode and cathode, as discussed in the context of Eqs. (18)–(20).

C. Simulated configuration

To simulate the system in Fig. 5 with the framework summarized by Eqs. (1)–(43), parameter values must be defined within a numerical-discretization approach. First, it is assumed that the diffusion constants of ions and electrons are the same ($\mathcal{D}_{e^-} = \mathcal{D}_{A^+}$), so as to avoid drastically differing diffusion timescales for ions and electrons (see Ref. 64). In this respect, it is important to emphasize that the equilibration time for any such system can be generally

characterized by a time constant such as

$$\tau = \frac{L^2}{2\mathcal{D}_{e^-}} = \frac{L^2}{2\mathcal{D}_{A^+}}. \quad (44)$$

For example, if all the ions were allowed to diffuse from the anode to the cathode through an *electrically conductive* separator, after being piled up in isolation within a region of width L_a in Fig. 5, then it would take approximately time τ to reach an equilibrated constant ion density across the entire length L . To capture equilibrium and nonequilibrium properties, per Eqs. (25)–(32), a finite-difference grid is employed with a spacing of Δx and a time step of Δt . Full numerical details can be found in the Supplemental Material [44] (see also Refs. [63,64]). The finite-difference grid resolution should be roughly

one tenth the screening length (L_s) of the mobile ions and electrons in the manner of $\Delta x < L_s/10$, where $L_s = \sqrt{\epsilon k_B T / q^2 \rho_{\max}}$. For a fixed-current flux (J), the mean velocity v of carrier transport does not change appreciably as the system size (L) is scaled, so long as the ρ_{A^+} and ρ_{e^-} densities are held fixed. Thus, through the Courant-Friedrichs-Lewy condition $\Delta t \leq \Delta x / v$, one ends up with a total number of continuity-equation time steps that scales as $N_{\text{steps}} = \tau / \Delta t \propto L^2$. To some extent, the current flux can be increased proportionally to overcome this limitation and a variable real-space grid (Δx) can be employed to alleviate the increasing simulation size with dimensionality (L). However, the simulation dimension is not particularly important for this study, since the trends are generalizable through the scaling relation in Eq. (44).

Hence, to simplify the numerical considerations, the results are presented for a “mesoscopic battery” dimension of $L = 0.2 \mu\text{m}$. The ion and electron concentrations are set to the maximum value of $\rho_{\max} = 0.25 \text{ mol/L}$ such that the direct impact of interfacial phenomena can be readily visualized. One could model larger dimensions ($L > 1 \mu\text{m}$) and higher charge densities ($\rho_{\max}$), but the screening length to device length ratio (L_s/L) needs to be preserved to conceptualize operation across the whole system simultaneously in the context of a quasielectric field ($\mathcal{E}_{A^+}$). Otherwise, competing drift and diffusion properties cannot be presented across the entire device in one plot. Hence, to readily visualize interfacial properties, one either moves toward a less practical device length ($L < 1 \mu\text{m}$) with reasonable charge storage densities ($\rho_{\max}$) or toward a more reasonable device length ($L \gg 1 \mu\text{m}$) with even less realistic charge storage densities ($\rho_{\max}$). We have opted for the former as, again, our focus is on general physical trends. For further details on advanced numerical methods, see Refs. [25–27].

Within the separator-electrolyte region ($L_a < x < L_c$) in Fig. 5(a), an immobile fixed electron density of $\rho_{\max}/10$ is placed. Its concentration is set lower simply to aid its visualization and the impact of carrier density on operational properties in the results presentation of this paper within the separate regions—alternative higher density values could have also been chosen. The junction widths are set such that $L_a = L - L_c$ and $(L_c - L_a)/L = 0.2$, as shown in Fig. 6(a) [68–70]. The internal energy per ion parameters, per Eqs. (33) and (34), are outlined in the Supplemental Material [44] and provide the profile given in Fig. 6(a) [54]. By further assuming a $\epsilon_{\text{rdx}|a} - \epsilon_{\text{rdx}|c} = 80k_B T$, one obtains the voltage profile in Fig. 6(b) via Eqs. (6)–(15) and Eqs. (35)–(43). These values have been selected to readily observe the voltage contribution from the ionic term in the form of $(\epsilon_{A^+|a} - \epsilon_{A^+|c})/(\epsilon_{\text{rdx}|a} - \epsilon_{\text{rdx}|c}) = 1/4$. Other values could have been selected with no loss of generality. A summary list of all parameter settings, including their physical meaning, can be found in the Supplemental Material [44] (see also Refs. [51,52,54,71]).

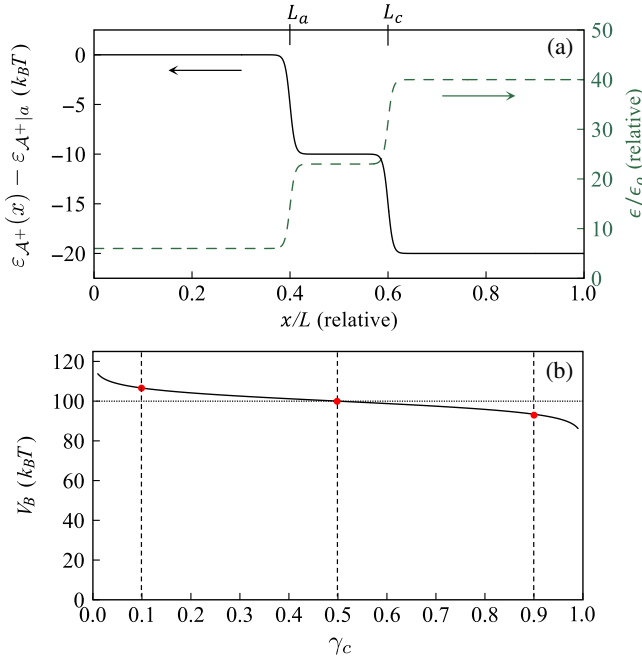


FIG. 6. (a) The assumed distribution of the internal energy per alkali ion (ϵ_{A^+}) referenced against the bulk internal energy in the anode ($\epsilon_{A^+|a}$) across a total length of $L = 0.2 \mu\text{m}$. The anode, separator-electrolyte, and cathode regions are marked at L_a and L_c , respectively. The internal energy per alkali ion in the electrolyte is set midway between that of the anode and cathode $\epsilon_{A^+|s} = (\epsilon_{A^+|a} + \epsilon_{A^+|c})/2$, with a smooth gradient of variation between each region—details are given in the Supplemental Material [44]. On the right axis in green (dashed line) is the corresponding dielectric constant variation (ϵ) that facilitates the spatial variation in ϵ_{A^+} for the model system selected—with ϵ_0 being the permittivity of free space. (b) The voltage profile as a function of the ion filling fraction in the cathode (γ_c) for the system in Fig. 5, with $(\epsilon_{A^+|a} - \epsilon_{A^+|c})/(\epsilon_{\text{rdx}|a} - \epsilon_{\text{rdx}|c}) = 0.25$. Points that are later investigated for ion-equilibrium, charging, and discharging trends are marked in red. All energy units are displayed in $k_B T$, with $T = 300 \text{ K}$.

The operational points marked with a red circle in Fig. 6(b) will be studied under ionic equilibrium, discharging, and charging.

IV. RESULTS AND DISCUSSION

A. Ionic equilibrium

To conceptualize the operation of such a battery within the proposed framework, let us return to the first three questions raised at the end of Sec. II A concerning ionic equilibrium. To begin with, consider the charge distributions in Figs. 7(a)–7(c). These results are obtained by first setting a uniform fraction of charge occupation of $\gamma_a \rho_{\max}$ in the anode and $\gamma_c \rho_{\max} = (1 - \gamma_a) \rho_{\max}$ in the cathode. Recall that the full configuration is detailed in Sec. III C and Figs. 5–6. From these instantaneous initial conditions, the system is then allowed to equilibrate following Eqs. (25)–(32). The ion density (ρ_{A^+}) is allowed to freely diffuse throughout $0 < x < L$, while each mobile electron concentration ($\rho_{e^-|a}$ and $\rho_{e^-|c}$) is restricted to move in its respective anode and cathode regions. The primary driving force toward ionic equilibrium is the quasielectric field ($\mathcal{E}_{A^+}$) established by ε_{A^+} and given in Fig. 6(a) (again see Sec. II B). A second driving force arises from the entropy term for ions given in Eq. (35), which in turn leads to $J_{A^+|\text{diff}}$ in Eq. (25). Both factors contribute to determining the distinct final charge configurations in Figs. 7(a)–7(c). In all cases, away from the anode-separator and separator-cathode interfaces, the electron and alkali-ion concentrations are in precise balance, in accordance with the principle of charge neutrality.

However, under ionic equilibrium conditions at each interface, there is an accumulation and depletion of charge. For each charge-state configuration, this trend can be seen in Figs. 7(d)–7(f), where the summation of all charges is plotted per Eq. (30)—again, minor differences emerge between the three results due to entropy (or concentration) trends across the three configurations. Notably, in all cases net positive charge builds up to the right of each junction and net negative charge to the left: this in turn creates an electrostatic potential ϕ per Eq. (29) that can be seen in Figs. 7(g)–7(i). Juxtaposed against ϕ (black) is the absolute value of the internal energy per alkali ion ($|\varepsilon_{A^+}|$ in dashed purple), through which it can be seen that ϕ arises to oppose ε_{A^+} within the action of $J_{A^+|\text{diff}}$ in Eq. (25) [see also Fig. 6(a)].

Yet, ϕ and $|\varepsilon_{A^+}|$ are never identical in Figs. 7(g)–7(i). This is because ϕ also works to counter the diffusion current $J_{A^+|\text{diff}}$ in Eq. (25). In the case of Fig. 7(g), where $\gamma_a = 0.9$ and $\gamma_c = 0.1$, there is an immediate change in the electron concentration ($\rho_{e^-|a}$ and $\rho_{e^-|s}$) by a factor of 9 at the anode-separator interface, which leads to a further ϕ contribution of $k_B T \ln(9)$ at this junction. Similarly, in Fig. 7(h), where the charge state is equal in the anode and cathode, the concentration lowers by 5 from the anode to

the separator, yielding a ϕ increase of $k_B T \ln(5)$ and then, correspondingly, rises again by a factor of 5 at the cathode, again leading to a lower ϕ rise at this second interface by $-k_B T \ln(5)$. While in Fig. 7(i) the charge-state symmetry is opposite to that of Fig. 7(g), with $\gamma_a = 0.1$ and $\gamma_c = 0.9$, yielding a reduction of ϕ at the separator-cathode interface of $-k_B T \ln(9)$ as compared to $|\varepsilon_{A^+}|$.

The manner in which ϕ works to counter both entropic (concentration) and internal energy per ion (ε_{A^+}) spatial variations fundamentally gives rise to a balance of the alkali-ion (A^+) flow across the entire system, as can be seen in Figs. 7(j)–7(l). Here, a direct balance of drift ($J_{A^+|\text{drift}}$) and diffusion ($J_{A^+|\text{diff}}$) ionic currents across each interface is evident and provides for $J_{A^+} = 0$ under ionic equilibrium. Outside of each interface, that of the anode-separator and separator-cathode, there is neither a drift nor a diffusion current. However, within each interface, the two are in direct balance so as to attain ionic equilibrium. It is this zero-current balance between the drift and diffusion contributions to J_{A^+} per Eq. (25) in Figs. 7(j)–7(l), as well as the corresponding formation of charge accumulation and depletion regions at each junction in Figs. 7(a)–7(f), that renders the operation of rocking-chair batteries analogous to that of a p - n junction diode and related semiconductor devices [8,16,17]. Indeed, for these reasons, p - n junction devices are often referred to as drift-diffusion devices. In the same manner, one can consider an alkali-ion (A^+) rocking-chair battery to be a drift-diffusion device, thereby borrowing further upon semiconductor-device concepts that began with the quasielectric field ($\mathcal{E}_{A^+}$) concept introduced in Secs. II B–II C and implemented via Eqs. (25)–(32).

B. Discharging

Moving on from ionic equilibrium, we shall now examine fully nonequilibrium properties by first addressing discharging characteristics in the context of the two final questions posed at the end of Sec. II A. Numerically, it is easier to study discharging under constant-current conditions, as illustrated in Fig. 1(a). This is accomplished by removing an electron density of $|J_{\text{ext}}| \Delta t / \Delta x$ from the anode-electrode interface and placing it at the cathode-electrode interface in each time-step (Δt) iteration of Eqs. (25)–(32) (for further details, see the discussion in Sec. III). Here, J_{ext} is the target current density for discharging at the external (*ext*) electrodes and is defined as

$$|J_{\text{ext}}| = \frac{L_a \rho_{\max}}{\zeta \tau}, \quad (45)$$

where $\zeta \geq 1$ is a multiplying factor that determines the discharging rate in terms of the system time constant (τ) given in Eq. (44). Under these current-flow boundary conditions, when $\zeta = 1$, the steady-state discharging profiles given

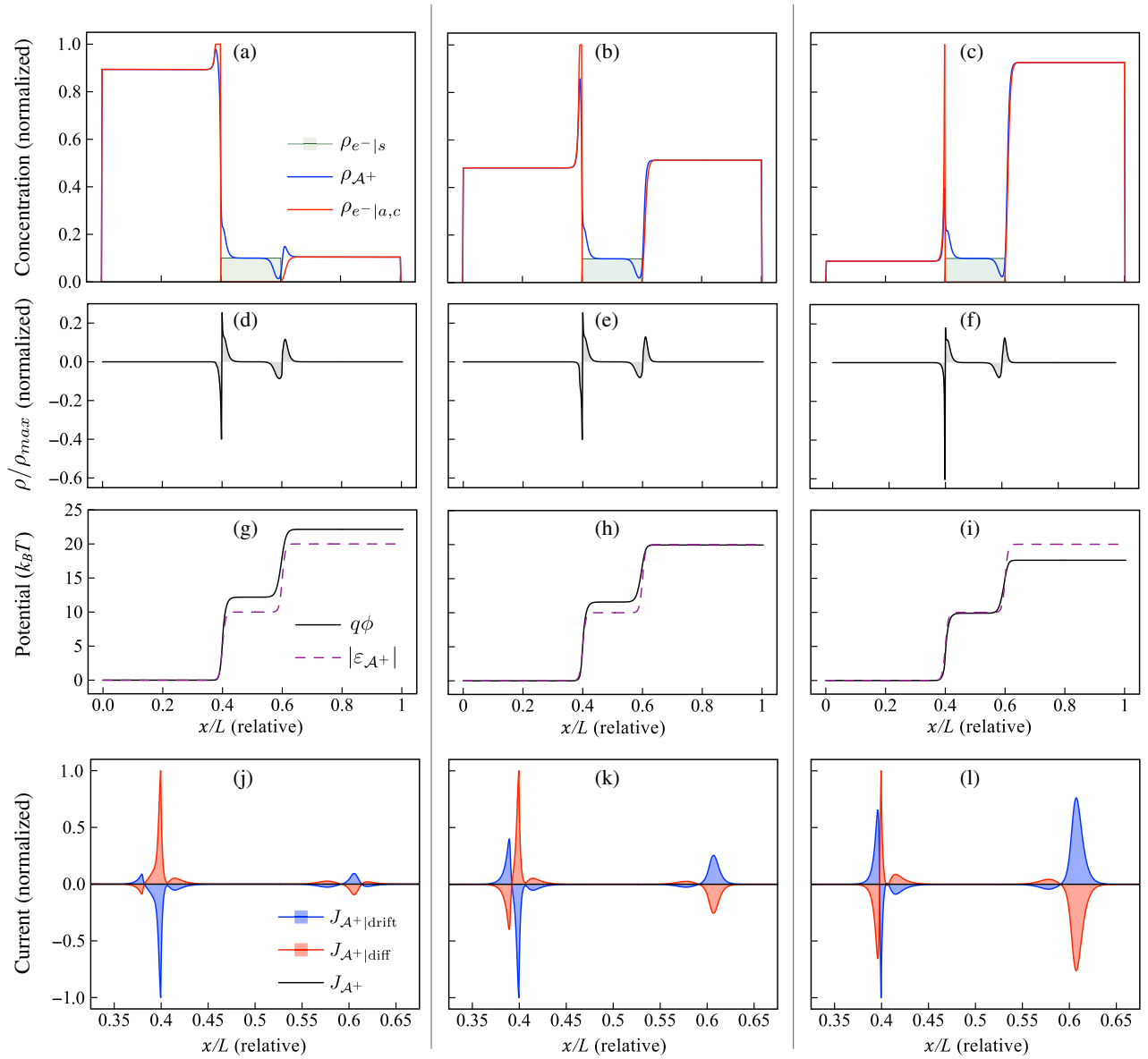


FIG. 7. The ionic equilibrium properties for various states: (a),(d),(g),(j) 90% charged ($\gamma_a = 0.9$, $\gamma_c = 0.1$), (b),(e),(h),(k) 50% charged ($\gamma_a = 0.5$, $\gamma_c = 0.5$), and (c),(f),(i),(l) 90% discharged ($\gamma_a = 0.1$, $\gamma_c = 0.9$). (a)–(c) The charge distributions with the anode on the left ($0 \leq x/L \leq 0.4$) and the cathode on the right ($0.6 \leq x/L \leq 1$). The separator-electrolyte region and its fixed negative charge ($\rho_{e^-|s}$) is shaded in green ($0.4 \leq x/L \leq 0.6$). The alkali-ion charge (ρ_{A^+}) is shown in blue, while the mobile electron density in the anode and cathode is shown in red ($\rho_{e^-|a}$ and $\rho_{e^-|c}$). All charge storage concentrations are normalized by $\rho_{\max}$. (d)–(f) The net charge distribution under ionic equilibrium for each charge state per Eq. (30). (g)–(i) The electrostatic potential ϕ arising under each of the ionic equilibrium charge distributions and the corresponding internal-energy magnitude per alkali ion ($|\varepsilon_{A^+}|$). (j)–(l) The drift and diffusion currents for the alkali ions counterbalancing under ionic equilibrium: outside the plotted region, all currents ($J_{A^+|drift}$, $J_{A^+|diff}$, and J_{A^+}) are zero. Positive current flow is from left to right inside the battery ($0 \rightarrow L$).

in Figs. 8(a)–8(c) are obtained. All such steady-state discharging results have been obtained by first reaching ionic equilibrium at $[\gamma_a]_{\text{ion-eq}} = [\gamma_a]_{\text{neq}} + 0.05$ and then allowing the boundary-condition discharging current (J_{ext}) to flow over successive numerical iterations of Δt until γ_a reaches the target nonequilibrium (neq) value of $[\gamma_a]_{\text{neq}}$

given in the upper portion of each panel in Fig. 8. The discharging interval of $[\gamma_a]_{\text{ion-eq}} - [\gamma_a]_{\text{neq}} = 0.05$ has been found to work well; discharging toward steady-state over a larger interval does not discernibly change the results presented in Fig. 8. Moreover, the fixed-current boundary-condition approach summarized by Eq. (45) could also be

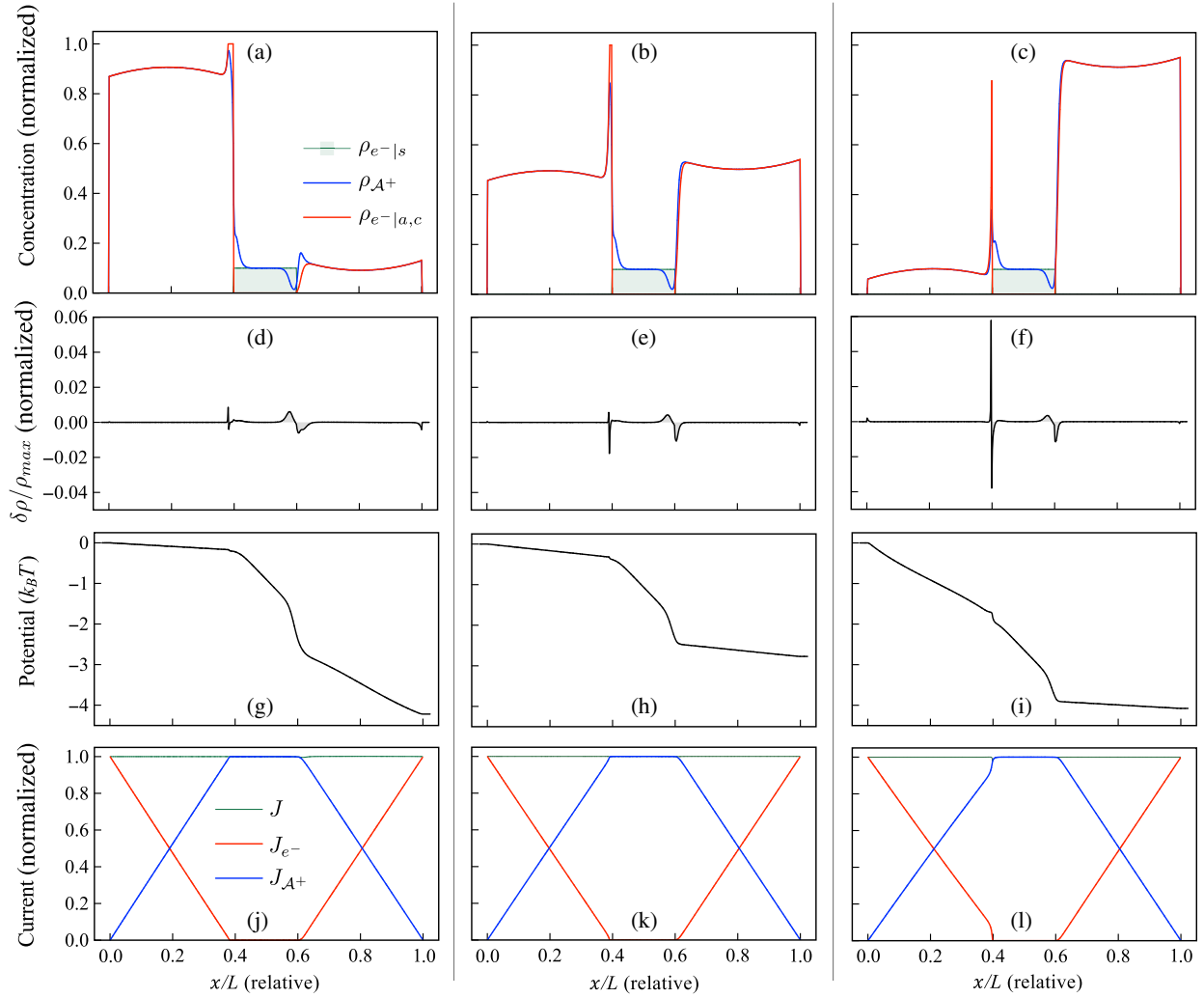


FIG. 8. The internal nonequilibrium (neq) properties for various net charge states at a fixed discharging current: (a),(d),(g),(j) 90% charged ($\gamma_a = 0.9$, $\gamma_c = 0.1$), (b),(e),(h),(k) 50% charged ($\gamma_a = 0.5$, $\gamma_c = 0.5$), and (c),(f),(i),(l) 90% discharged ($\gamma_a = 0.1$, $\gamma_c = 0.9$). (a)–(c) The charge distributions with the anode on the left and the cathode on the right. The separator-electrolyte region and fixed negative charge ($\rho_{e-|s}$) is shaded in green. The alkali-ion charge (ρ_{A+}) is shown in blue, while the mobile electron density in the anode and cathode is shown in red ($\rho_{e-|a}$ and $\rho_{e-|c}$). (d)–(f) The net charge redistribution from ionic equilibrium under the same net anode and cathode charge state: $\delta\rho = [\rho]_{\text{neq}} - [\rho]_{\text{ion-eq}}$. (g)–(i) The internal electrostatic potential $\delta\phi = [\phi]_{\text{neq}} - [\phi]_{\text{ion-eq}}$ arising during discharging current flow. (j)–(l) The discharging current flow (J) decomposed into electronic (J_{e-}) and ionic (J_{A+}) contributions normalized by J_{ext} . Positive current flow is from left to right inside the battery ($0 \rightarrow L$). All charge storage concentrations are normalized by ρ_{max} .

replaced by fixed-voltage boundary conditions; this would result in similar physical trends to those presented in this study per Ohm's law.

The results in Figs. 8(a)–8(c) represent a rather fast steady-state discharge rate; thus a nonequilibrium curvature in ρ_{e-} and ρ_{A+} is prominently visible away from the anode-separator and separator-cathode interfaces. However, these concentrations still largely follow each other away from separator-electrolyte interfaces, thus indicating a charge-balanced gain of electrons or ions at the cathode and a similarly charge-balanced loss of electrons or ions at the anode. Yet the overall uncompensated net

nonequilibrium charge perturbation defined by

$$\delta\rho = [\rho]_{\text{neq}} - [\rho]_{\text{ion-eq}} \quad (46)$$

is rather small and can be seen in Figs. 8(d)–8(f). To obtain physically meaningful results, the difference in Eq. (46) must be evaluated at the exact same values of $\gamma_a = 1 - \gamma_c$ under equilibrium and nonequilibrium conditions ($[\gamma_a]_{\text{ion-eq}} = [\gamma_a]_{\text{neq}}$). Its net effect is to produce the nonequilibrium potential perturbation

$$\delta\phi = [\phi]_{\text{neq}} - [\phi]_{\text{ion-eq}}, \quad (47)$$

the profile of which for the three target discharging configurations can be seen in Figs. 8(g)–8(i). These nonequilibrium screening properties directly emerge from the imposed steady-state current-injection criteria outlined in the context of Eq. (45) and illustrated in Fig. 1(a).

Crucially, the direction of $\delta\phi$ in Figs. 8(g)–8(i) is opposite to that of ϕ , as given under ionic equilibrium conditions in Figs. 7(g)–7(i). This means that they represent the action of internal resistance in response to current flow within the battery device and thereby lower the overall total voltage under active operation seen by electrons flowing through the external circuit per Eqs. (9)–(13) [22–24,72]. In this example, a rather large discharge current (via $\zeta = 1$) has been selected, so the overall impact of $\delta\phi$ is on the order of $4k_B T$ [cf. Figs. 6 and 7(g)–7(i)]. With much lower discharge rates ($\zeta \gg 1$), the corresponding impact of $\delta\phi$ is proportionally reduced; under an infinitesimally small discharge current, one obtains the voltage profile in Fig. 6(b). However, this internal-resistance analysis excludes any additional sharp interfacial potential drop (and thus additional internal resistance) at the electrodes that might be further needed to sustain J_{ext} via the redox charge-transfer rates [34,64]. The conditions governed by Eq. (40) are not general to all anode and cathode materials, but particular to the model redox system selected. Nevertheless, detailed further work on optimizing such systems should not exclude these aspects from future consideration.

The potential-drop ($\delta\phi$) properties emerging from internal-resistance contributions present in the bulk of the anode, cathode, and separator-electrolyte are intimately tied to current flow throughout these regions. In Figs. 8(j)–8(l), we see the decomposed electron and ion currents (J_{e^-} and J_{A^+} , in red and blue, respectively) [27]. Importantly, current conservation dictates a near-fixed total current J per Eq. (32), with any minor deviation arising from the necessary transfer of charges from the anode to the cathode during discharging. This near-constant total current [J , green line in Figs. 8(j)–8(l)] results in the ion current (J_{A^+} , blue) expectedly dominating and maximizing in the separator-electrolyte while similarly decaying toward the external electrodes—demonstrating that this approach reproduces the findings of earlier continuity-equation battery models [25,26]. Correspondingly, the electron current (J_{e^-} , red) maximizes at the electrodes and then decays to zero at each separator-electrolyte interface. This trend is repeated with only small variations between all three charge states provided in Figs. 8(j)–8(l). Interestingly, the nonequilibrium current flow can also be expressed in terms of nonequilibrium electrochemical potentials in a similar manner to how current flow is described by quasi-Fermi levels in the electronic device literature (see the Supplemental Material [44] (see also Refs. [17,22–24])).

Now, the variation in the potential-drop distribution in each region [anode, cathode, and electrolyte per Figs.

8(g)–8(i)] can be worked out by recalling the electronic (e^-) and ionic (A^+) conductivity relations given by [24]

$$\sigma_{e^-} = q\rho_{e^-}u_{e^-}, \quad (48)$$

$$\sigma_{A^+} = q\rho_{A^+}u_{A^+}. \quad (49)$$

Moreover, since we are assuming equivalence of the electronic and ionic mobilities $u_{e^-} = u_{A^+}$ per the discussion in Sec. III, the primary variation in conductivity between regions arises from variation in the carrier charge densities ρ_{e^-} and ρ_{A^+} . In all three charge configurations in Figs. 8(a)–8(c), the separator-electrolyte has between 9 and 5 times less the charge density of the anode and cathode regions but half the length, and thus absorbs proportionally more of the voltage drop relative to the lengths and carrier densities of all other regions in Figs. 8(g)–8(i). Correspondingly, when the anode (cathode) has 9 times the charge density of the cathode (anode) in Figs. 8(g) and 8(i), we see the region with the lower conductivity absorbing proportionally more of the nonequilibrium ($\delta\phi$) potential drop. A more in-depth analysis along these lines follows next, in Sec. IV C.

C. Charging

Let us now turn to charging properties in the context of the nonequilibrium questions posed at the end of Sec. II A. Numerically, this is readily accomplished by an approach exactly the opposite of the one detailed at the start of Sec. IV B via a constant-current source, as illustrated in Fig. 1(b). That is, at each time step (Δt) iteration of Eqs. (25)–(32), an electron charge density equal to $|J_{\text{ext}}|\Delta t/\Delta x$ is removed from the cathode-electrode interface and placed at the anode-electrode interface. Thus, following symmetry principles, one obtains nonequilibrium steady-state distributions of the form given in Figs. 9(a)–9(c). Here, one sees a curved accumulation of charge (ρ_{e^-} and ρ_{A^+}) in the anode bulk and a similar curved depletion of charge from the cathode bulk—compare Figs. 9(a)–9(c) with Figs. 7(a)–7(c). The steady-state results in Fig. 9 are obtained by accumulating anode charge from an ionic equilibrium reference configuration set at $[\gamma_a]_{\text{ion-eq}} = [\gamma_a]_{\text{neq}} - 0.05$ until the target charging value of $[\gamma_a]_{\text{neq}}$ is reached (as indicated at the top of each panel in Fig. 9).

For each charging-state panel in Fig. 9, one can resolve the net uncompensated nonequilibrium charge-density perturbation ($\delta\rho$) via Eq. (46) as shown in Figs. 9(d)–9(f). Here, equal and opposite symmetry can be seen in relation to the discharging results in Figs. 8(d)–8(f). Again, nonequilibrium findings are only resolvable when differences are taken for the quantity of charge in the manner of $[\gamma_a]_{\text{neq}} = [\gamma_a]_{\text{ion-eq}}$. Correspondingly, the nonequilibrium potential-drop ($\delta\phi$) charging trends in Figs. 9(g)–9(i) also display equal and opposite symmetry to the discharging trends in Figs. 8(g)–8(i). In particular, the overall change

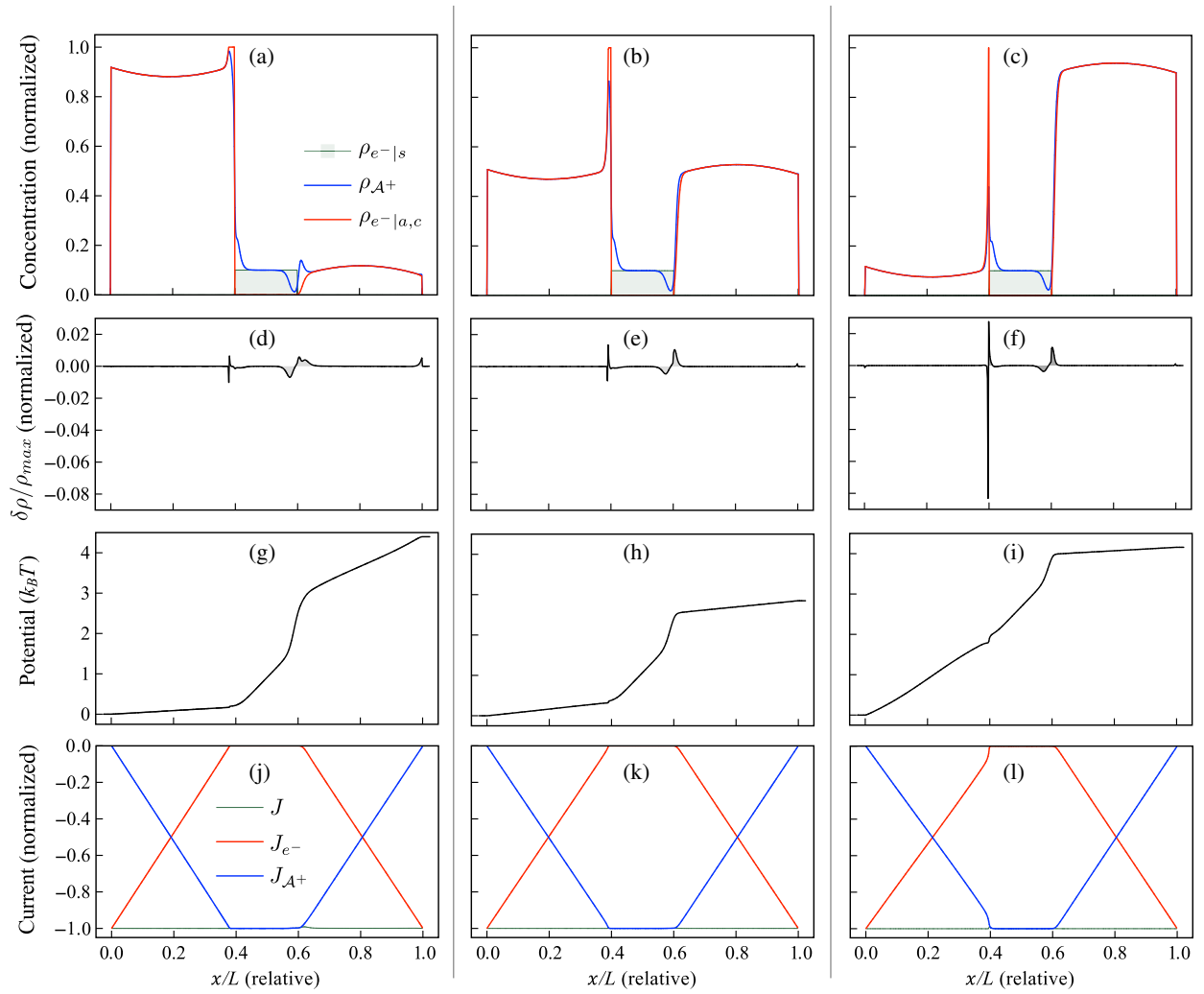


FIG. 9. The internal nonequilibrium (neq) properties for various net charge states at a fixed charging current: (a),(d),(g),(j) 90% charged ($\gamma_a = 0.9$, $\gamma_c = 0.1$), (b),(e),(h),(k) 50% charged ($\gamma_a = 0.5$, $\gamma_c = 0.5$), and (c),(f),(i),(l) 90% discharged ($\gamma_a = 0.1$, $\gamma_c = 0.9$). (a)–(c) The charge distributions with the anode on the left and the cathode on the right. The separator-electrolyte region and fixed negative charge ($\rho_{e^-|s}$) is shaded in green. The alkali-ion charge (ρ_{A^+}) is shown in blue, while the mobile electron density in the anode and cathode is shown in red ($\rho_{e^-|a}$ and $\rho_{e^-|c}$). (d)–(f) The net charge redistribution from ionic equilibrium under the same net anode and cathode charge state: $\delta\rho = [\rho]_{\text{neq}} - [\rho]_{\text{ion-eq}}$. (g)–(i) The electrostatic potential $\delta\phi = [\phi]_{\text{neq}} - [\phi]_{\text{ion-eq}}$ arising during charging internally within the battery. (j)–(l) The charging current flow (J) decomposed into electronic (J_{e^-}) and ionic (J_{A^+}) contributions. Positive current flow is from left to right inside the battery ($0 \rightarrow L$). All charge storage concentrations are normalized by ρ_{max} .

in the potential drop is on the order of $4k_B T$ in the same direction as the equilibrium electrostatic profiles in Figs. 7(g)–7(i). This means that a potential greater than the equilibrium voltage of the battery [per the plot in Fig. 6(b)] must be applied to overcome internal resistance in the battery and transfer charge from the cathode to the anode. The size of the additional potential needed depends proportionally on the driving-current magnitude at which charging is being attempted ($|J_{\text{ext}}|$). Of course, as discussed in Sec. IV C, for this particular redox system there may be additional electrode interfacial resistance contributions so as to sustain the necessary current (J_{ext}), that then possibly further increases the required excess potential directly at

the metal-electrode interfaces. Again, to restrict our discussion to more general aspects, this is left to a future detailed study. The point is that the concept of an excess potential needed to drive the charging of a battery is directly emergent from the physics expressed in Eqs. (25)–(32) and compatible with the concept of a quasidelectric field acting on ions as discussed in Sec. II B.

The internal current flux inside this model battery system under charging conditions is given in Figs. 9(j)–9(l) and can be seen to be equal and opposite to that of Figs. 8(j)–8(l). Once again, the ion current (J_{A^+} , blue) peaks in the separator-electrolyte and then decays linearly toward zero at the electrodes; while the electron current (J_{e^-} ,

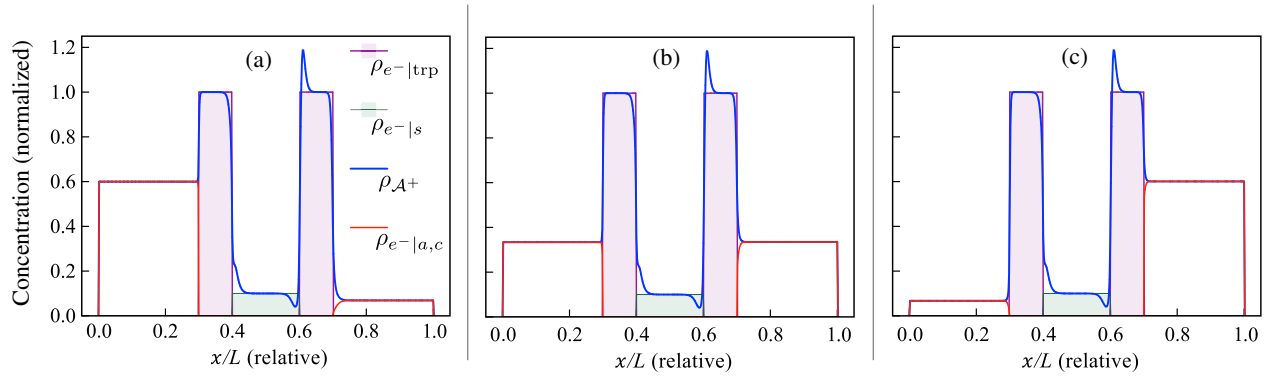


FIG. 10. An example of ionic equilibrium properties for various net charge states in a battery system subject to interfacial capacity loss (purple): (a) 90% charged ($\gamma_a/\gamma_c = 9$), (b) 50% charged ($\gamma_a/\gamma_c = 1$), and (c) 90% discharged ($\gamma_c/\gamma_a = 9$). The charge distributions are shown with the anode on the left and the cathode on the right. The separator-electrolyte region and fixed negative charge ($\rho_{e^-|s}$) is shaded in green. The fixed (or trapped) electron density, arising due to parasitic redox reactions ($\rho_{e^-|trp}$), is shown in purple. The mobile alkali-ion charge (ρ_{A^+}) is shown in blue, while the mobile electron density in the anode and cathode is shown in red ($\rho_{e^-|a}$ and $\rho_{e^-|c}$). The formation of a capacity-loss region is assumed to not alter the internal energy per A^+ ion (ε_{A^+}) distribution from that given in Fig. 6(a). All charge storage concentrations are normalized by ρ_{max} .

red) similarly peaks at the electrodes to satisfy $J_{ext} = J_{e^-}$ and decays to zero at the anode-electrolyte and cathode-electrolyte interfaces [27]. The total current (J , green) in Figs. 9(j)–9(l) rarely deviates from the injected value J_{ext} , except to facilitate the net transfer of charge from the anode to the cathode per Eqs. (26) and (28). In Figs. 9(g)–9(i), the internal current flow (J) and nonequilibrium potential drop properties ($\delta\phi$) are once more coupled through the conductivity expressions in Eqs. (48) and (49) and their relationship follows the same general reasoning as given at the end of Sec. IV B. Rather than repeat that line of argumentation, it is useful to extrapolate these trends toward more general battery properties.

Of particular interest is the overall time taken to charge a battery [72]. If a battery were instead constructed with a “macroscopic” dimension of $L = 500 \mu\text{m}$ [68–70], then to charge in 300 s (or 5 min), the average diffusion constant per Eq. (45) should be $\mathcal{D} \approx 4 \times 10^{-6} \text{ cm}^2/\text{s}$ [71,73]. For the sake of simplicity, this assumes $\mathcal{D} = \mathcal{D}_{e^-} = \mathcal{D}_{A^+}$ as throughout this study. Within this assumed total internal length of $L = 500 \mu\text{m}$ as depicted in Fig. 5, realistic dimensionality estimates result in an anode width of $L_a \approx 200 \mu\text{m}$, an separator-electrolyte width of $L_c - L_a \leq 100 \mu\text{m}$, and a cathode width of $L - L_c \approx 200 \mu\text{m}$ [68–70]. Now, since current conservation gives rise to a largely fixed total value of J throughout a charging battery [as discussed previously and shown in Figs. 9(j)–9(l)], the benefit of an electrolyte region that exceeds this diffusion range (approximately $4 \times 10^{-6} \text{ cm}^2/\text{s}$) by more than an order of magnitude seems largely irrelevant in the context of very fast charging. Ultimately, the charging and discharging time depends on the current flux sustained through the entire system (i.e., how quickly charge can be moved). If any single region has a

significantly lower diffusion constant, its resistive properties will dominate the charging time. The distinct manner in which the electron current maximizes at the electrodes [see J_{e^-} , red, in Figs. 9(j)–9(l)] means that poor electron transport ($\mathcal{D}_{e^-} \ll \mathcal{D}_{A^+}$) can become extremely limiting to charging and discharging performance—as has been emphasized early on in LiFePO_4 cathode development [74,75]. Conversely, ion transport is not merely restricted to the separator-electrolyte region [see J_{A^+} , blue, in Figs. 9(j)–9(l)]. Though it reaches a maximum in the separator-electrolyte, per the dictates of current conservation, it continues on to rather high values well into the anode and cathode, and thus $\mathcal{D}_{A^+}$ is of near-equal importance in those regions. Any region with very low ionic diffusivity can have a substantial impact on increasing the charging time by creating a high internal resistance.

In this context, one can counter argue that it is really conductivity (or its inverse, resistivity) that matters and not diffusion constants [see Eqs. (48) and (49)]. Yet, in conventional batteries one typically does not charge more than 90% or discharge to more than 10% of overall capacity [76]. This is done to avoid capacity loss via parasitic reactions [76]. Thus the contribution of the carrier density to overall conductivity (σ_{A^+} and σ_{e^-}) differences will not be much more than an order of magnitude between any one region of the battery (anode, separator-electrolyte, and cathode). Hence, fast charging requires suitably high diffusion constants for charge carriers in all regions, not merely in the separator-electrolyte, as per the recent focus on developing solid-state electrolytes [8,49,72]. On the other hand, for every decade of time [$\times 10$ multiple of ζ in Eq. (45)] that one can afford to wait for charging a battery, the required diffusion constant correspondingly decreases by a decade per Eq. (44). Hence, a 50-min charging time

requires an approximate diffusion constant on the order of approximately $4 \times 10^{-7} \text{ cm}^2/\text{s}$ when $L \approx 500 \text{ }\mu\text{m}$ and so on. Nonetheless, the specifics of diffusion will invariably become quite complex in composite structures [49,72,76]. Thus, this physical reasoning is intended to serve only for the purposes of general intuitive guidance.

D. Capacity loss

After repeated discharging and charging cycles, capacity loss is often manifest within alkali-ion ($\mathcal{A}^+$) rocking-chair batteries [76]. From a chemical perspective, it is generally agreed that parasitic redox reactions at the cathode-electrolyte and anode-electrolyte interface are responsible for this loss [77]. Though sophisticated phase-dependent models do exist [9], the general physics of capacity loss can also be understood through the trapping or binding of ions ($\mathcal{A}^+$) and/or electrons. Under the principle of charge compensation, only one carrier needs to become immobile for the opposite carrier to be rendered similarly inutile. This is readily demonstrated within the framework of Eqs. (25)–(32) and captured by the ionic equilibrium plots presented in Figs. 10(a)–10(c). Here, two regions of width $0.1L$ have formed on each side of the separator-electrolyte whereby all the redox sites with density ρ_{max} have been transformed, by way of the aforementioned parasitic reactions, to immobile electron (e^-) trap sites (shaded in purple). Due to this trapping process, electron conduction is considered severely inhibited in this region (treated as null in this approximation). However, no mobility limits have been placed on the corresponding $\mathcal{A}^+$ ions—they are left free to diffuse in all regions with an unimpeded equivalent diffusion constant $\mathcal{D}_{\mathcal{A}^+}$. Nevertheless, for the three distinct charge states presented in Fig. 10 (including 90% charged, 50% discharged, and 90% discharged), it can be seen that a near-equal concentration of $\mathcal{A}^+$ ions ($\rho_{\mathcal{A}^+}$, blue) remains bound within the capacity-loss region. Despite their preserved mobility, $\mathcal{A}^+$ ions must remain to compensate the trapped electron concentration (purple shaded in Fig. 10); otherwise, excessive electric fields would build up. Any deviation of $\mathcal{A}^+$ from the trapped electron concentration in Figs. 10(a)–10(c) is merely present to facilitate the interfacial entropy and internal energy per ion variations ($\varepsilon_{\mathcal{A}^+}$) discussed earlier in Sec. IV A.

Of course, capacity loss need not be restricted to electron trapping. By the same reasoning, trapped or chemically bound $\mathcal{A}^+$ ions would also require a similar compensating electronic charge density. Hence, the reasoning is general: any reaction that binds either charge (e^- or $\mathcal{A}^+$) renders its opposite charge inutile and a casualty of capacity loss. Electron trapping is only provided in Fig. 10 as a demonstration of this general charge-compensation principle. In either case, capacity loss is most dramatically evident in those regions that remain actively available for charge storage. For example, to the left and the right of

those regions, where carriers have become bound (purple) in Figs. 10(a)–10(c), comparably fewer charges are available for storage than shown in the original pristine configurations in Figs. 7(a)–7(c). In this manner, device modeling is not only useful in understanding discharging and charging but also capacity-loss mechanisms. To provide more dynamical insights, future work might focus on further coupling the methodology in Sec. II with rate equations describing the chemical mechanisms underpinning capacity loss [9,63,76,77].

V. CONCLUSIONS

In this work, we have sought to further extend those drift and diffusion current-flow concepts that underpin the operation of semiconductor devices into the realm of rocking-chair alkali-ion batteries [11,12,16,17,20]. This has been accomplished by introducing the concept of a quasielectric field acting on ions at each interface in a double junction formed from an anode, an separator-electrolyte, and a cathode [20]. The quasielectric field has been shown to originate from the internal-energy variation per ion particle within the electrochemical potential across each junction, and this has been further correlated with a vacuum reference in an analogous manner to carrier properties in the electronic device literature [16,17]. When ions equilibrate across such a double junction but electron conduction is suppressed, taking a redox polymer battery as a model system, this has been shown to give rise to the total voltage experienced by electrons via both their own intrinsic electrochemical potential offset and the further offset provided by the potential formed by ions when equilibrating [14,66]. Ionic equilibration itself has been found to be manifest through the balance of drift and diffusion ion flow, providing a direct physical analogy to p - n junctions in the electronic device literature. In a similar manner to earlier semiclassical descriptions of rocking-chair alkali-ion batteries [24,25,27], further properties have been shown to be emergent from the resulting continuity-equation formulation in the context of drift and diffusion including: internal-resistance losses during charging and discharging, nonequilibrium carrier profiles, transitions between electron flow and ion flow in the total current, characteristic charging and discharging times, and capacity loss. Overall, the conceptualization presented has aimed to draw closer the domains of electronic device modeling and electrochemical device modeling in the solid-state physics literature. Crucially, it does not seek to replace existing continuity-equation descriptions of rocking-chair batteries [22,23,26], but to instead provide a complementary approach that is relatable to drift-diffusion electronic device models common in the solid-state literature [16,17,20].

Future work should aim to further generalize its application. This includes not only first-principles justifications,

and refinement of the assumptions adopted (including ionic configurations), but also the incorporation of such models within chemical kinetics and even dynamical phase-field methods [9,63]. Direct comparison with the galvanostatic intermittent titration technique, such that diffusion properties arising from ion-lattice interactions are captured, would be especially important in future work along these lines [78]. Multiscale extensions within the complex construction of modern rocking-chair batteries and metallic anodes should also be pursued [36], as well as capturing volumetric changes that are not necessarily insignificant [41]. Experimental correlation and possible validation in the domain of well-controlled solid-state interfaces, as well as strongly correlated solids [37,75], could also prove quite useful [7,8,13]. For example, particular care should be applied when extending this modeling method to the oxides and phosphates commonly employed in rocking-chair batteries [29,37,38,78]. For such solids, there is a mixture of redox and band-transport behavior, often generalized under the term of strongly correlated interactions, that includes phenomena such as polarons and ion-polaron interactions. Such systems would not be well described by the Gerischer-Hopfield framework, unlike more simple redox polymer groups, and modifications would be needed (such as a variation on the Holstein small-polaron-band model) [79]. These further extensions make for exciting horizons in the further integration of device physics and rocking-chair battery models.

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DATA AVAILABILITY

The data that support the findings of this paper are openly available [44]; embargo periods may apply.

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