Computational modeling of sodium-iodine secondary batteries

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Abstract

This paper develops a computational model and applies it to investigate the performance of a rechargeable battery that is comprised of a molten-sodium anode, a NASICON sodium-ion-conducting separator membrane, and a iodine-based cathode. The cathode compartment is comprised of a porous-carbon felt and an aqueous catholyte that supports an iodine redox process. The battery chemistry can be represented globally as $2\text{Na}^+ + 2\text{I}^- \rightleftharpoons 2\text{Na} + \text{I}_2$. The ion transport is represented in terms of a Nernst–Planck formulation that includes four mobile species within the catholyte, Na^+ , I^- , I_3^- , and I_2 . The charge transfer chemistry is modeled using a Butler–Volmer formulation. The model considers solubility limits and the potential precipitation of NaI and I_2 . Parameter studies investigate the influences of charge and discharge rates, total elemental iodine loading, and effective conductivity of the carbon-felt cathode.

Keywords:

Secondary battery, Molten-sodium, Iodine redox, Computational Modeling,

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1. Introduction

Molten sodium can serve as the anode for high-performance rechargeable battery technology. Of course, sodium is an inexpensive, earth-prevalent, non-toxic, environmentally friendly, material. The challenge is to develop compatible sodium-ion conducting separator membranes together with cathode materials and architectures. The present paper focuses on NASICON (Sodium super ionic conductor) as the electrolyte separator membrane and a cathode based on the I_3^-/I^- redox couple. Although performance depends on more detailed chemistry within the cathode, the overall reaction for the Na-I₂ battery can be written globally as

The objective this paper is to develop and apply a computational model that predicts battery performance. The model represents the coupled chemistry and transport within the anode, separator, and cathode. The underpinning theory and model development concentrates on the cathode, where the chemistry and transport is the most complex. The cathode structure is also the area where the performance depends on numerous design and operational tradeoffs.

Inasmuch as the sodium melting point is 98 °C, molten-sodium batteries must operate at elevated temperature. Depending on the separator and cathode technologies, the sodium melting point may not be the limiting factor in

21 setting the operating temperature. For example, higher temperatures may
 22 be needed to achieve suitable ion conductivity in the separator membrane.
 23 In any case, the requirement for elevated-temperature operation restricts op-
 24 portunities for practical application. Although Na-based technology may not
 25 be suitable for consumer automotive applications, it does offer opportunities
 26 for applications such as large-scale grid storage.

27 [Figure 1 about here.]

28 Figure 1 illustrates features of a Na-I₂ battery architecture, with the
 29 reaction arrows indicating discharge conditions. During discharge the sodium
 30 reacts electrochemically at the Na-NASICON separator interface, delivering
 31 Na⁺ ions into the separator and electrons through the molten sodium into
 32 the external circuit. The charge-transfer reaction may be stated as

33 As the battery discharges, the sodium level within the anode compartment
 34 decreases.

35 The Na⁺ produced at the Na-NASICON interface migrates through the
 36 NASICON membrane toward the cathode-NASICON interface. The dense
 37 NASICON membrane is a pure sodium-ion conductor, with negligible elec-
 38 tronic conductivity. Thus, in addition to Na⁺ conductivity, the NASICON
 39 serves as the electronic separator between the anode and cathode compart-
 40 ments.

41 The cathode compartment is filled with a porous carbon felt that is in-
 42 filtrated with an aqueous catholyte. The catholyte serves as a solvent for

43 Na^+ , I^- , I_3^- and I_2 . During discharge, electrons returning from the external
 44 circuit conduct from the cathode current-collector into the carbon felt. At
 45 the interfaces between the carbon felt and the catholyte the iodine is reduced
 46 to form iodide via a charge-transfer reaction as

47 Within the catholyte solution, the iodine can be combined with two iodide
 48 ions to form tri-iodide ions (i.e., $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$). To maintain charge neutral-
 49 ity within the catholyte, Na^+ must emerge from the separator and enter the
 50 catholyte solution. All the mobile ions must be spatially distributed within
 51 the catholyte so as to maintain local charge neutrality. Moreover, it is impor-
 52 tant that the elemental iodine concentration is such that NaI and I_2 remain
 53 in solution.

54 The I_3^-/I^- redox couple has the potential to be an excellent aqueous-based
 55 cathode for sodium-based batteries. The iodine has relatively low molecular
 56 weight, high solubility, highly reversible redox reaction rate, and a suitable
 57 redox potential. Iodine’s aqueous phase solubility is reasonably high because
 58 iodine can react with other iodides to form poly-iodides, with the tri-iodide
 59 ion being the dominate ionic species in the aqueous solution. Thus, relatively
 60 high I^- and I_2 concentrations can be used, leading to aqueous catholyte
 61 with high capacity and high energy density. With respect to the standard
 62 hydrogen electrode, the redox potential of the I_3^-/I^- couple is approximately
 63 0.536 V and the redox potential of the I_2/I^- couple is approximately 0.5335 V.
 64 These relatively low redox electric potentials are important to avoid undesired
 65 electrolysis of the aqueous solution, such as the oxygen evolution reaction

(OER), which occurs at the standard redox potential greater than 0.7 V in the aqueous NaI solution. The tri-iodide/iodide (I_3^-/I^-) redox couple in the aqueous catholytes has been studied for a variety of lithium-iodine batteries [1–4], including flow batteries [5, 6].

2. Mathematical model

The model is based on fundamental electrochemistry concepts. Charge-transfer reactions are represented in the Butler–Volmer form. Mixed-conducting transport is based on a Nernst–Planck model. In other words, the ion flux is governed by a Nernst–Planck relationship and electrostatic potentials obey the Gauss law. The cathode structure is composed of a porous electron-conducting material (e.g., carbon felt), with the pore volume filled with an aqueous catholyte solution. The solid volume of the porous cathode is assumed to be a high-conductivity electron conductor. The mobile species within the catholyte are Na^+ , I^- , I_3^- , and charge-neutral I_2 . In addition to charge-transfer chemistry at the electrode-electrolyte interfaces, homogeneous reaction is considered within the catholyte. The electrolyte separator membrane is assumed to be a pure Na^+ conductor (e.g., NASICON). The molten Na anode is assumed to be a high-conductivity electron conductor. Current collectors at the ends of the electrode compartments are connected to an external circuit that can control the charge and discharge current. The model considers the solubility of NaI and I_2 , and hence the possible deleterious precipitation of condensed compounds. Material properties are derived from prior literature wherever possible.

[Figure 2 about here.]

Figure 2 illustrates the governing equations, the computational domains on which they are applied, and the boundary conditions. The model must represent the electrostatic potentials in the electrode and electrolyte phases. It must also represent the species concentrations in the electrolyte phases. The electrostatic potential and the species concentrations are closely coupled through the system of conservation equations.

The transient model is implemented in a one-dimensional spatial setting, spanning from the anode current collector to the cathode current collector. The spatial operators are discretized using a conservative finite-volume approach. The system is solved computationally using the method of lines.

2.1. Catholyte concentrations

Considering the cathode's porous microstructure, the species (Na^+ , I^- , I_3^- , I_2) transport within the catholyte solution can be represented as

$$\frac{\partial \phi[X_k]}{\partial t} + \nabla \cdot \mathbf{J}_k = \phi \dot{\omega}_k + A_s \dot{s}_k, \quad (4)$$

where ϕ is the porosity (catholyte volume fraction) and $[X_k]$ are the species molar concentrations. The transport fluxes are represented in a Nernst-Planck formulation as

$$\mathbf{J}_k = -D_k^e \nabla[X_k] - \frac{z_k F}{RT} D_k^e [X_k] \nabla \Phi_{\text{el}}, \quad (5)$$

where Φ_{el} is the electrostatic potential in the catholyte solution phase, T is the temperature, R is the gas constant, and F is the Faraday constant. The mobile ions have charge z_k ($z_{\text{Na}^+} = 1$, $z_{\text{I}^-} = -1$, $z_{\text{I}_3^-} = -1$, $z_{\text{I}_2} = 0$). The effective porous-media diffusion coefficients are represented as D_k^e , which are

110 related to the bulk diffusion coefficients D_k (Sect. 3.1) as

$$D_k^e = D_k \phi^\gamma, \quad (6)$$

111 where γ is the Bruggemann exponent, which is typically $\gamma \approx 3/2$.

112 Species molar production rates due to homogeneous chemical reactions
 113 within the catholyte are represented as $\dot{\omega}_k$. The homogeneous chemistry can
 114 be represented globally in terms of iodine-iodide redistribution as $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$.
 115 The species molar production rates resulting from electrochemical reaction at
 116 the distributed electrode surfaces are represented as $\dot{s}_k$ and A_s is the specific
 117 interface area (i.e., surface area per unit volume). The charge-transfer chem-
 118 istry at cathode-catholyte interfaces can be represented globally as Eq. 3.
 119 Details of the chemistry are discussed subsequently (Sect. 4).

120 The catholyte domain spans the space between the NASICON and the
 121 cathode current collector (cf., Fig. 2). At the NASICON interface, all species
 122 fluxes vanish, except the Na^+ flux. At the cathode current-collector interface
 123 all species fluxes vanish. In other words, with the exception of Na^+ , all the
 124 catholyte-species boundary conditions may be represented as $\mathbf{n} \cdot \mathbf{J}_k = 0$,
 125 where $\mathbf{n}$ is the outward-pointing unit vector. At the NASICON interface,
 126 the boundary condition is

$$\mathbf{n} \cdot \mathbf{J}_{\text{Na}^+} = \frac{i_{\text{ex}}}{F}, \quad (7)$$

127 where i_{ex} is the specified current that is delivered to, or supplied by, the
 128 external circuit.

129 2.2. Cathode charge conservation

130 The cathode structure is comprised of a porous carbon felt (electrode)
 131 that is infiltrated with the catholyte solution (electrolyte). As illustrated

132 in Fig. 2, the cathode phase spans the domain between the NASICON and
 133 the cathode current collector. The carbon felt is a pure electronic conductor
 134 whose local electrostatic potential Φ_{ed} is governed by

$$\frac{\partial \rho_{\text{ed}}}{\partial t} + \nabla \cdot \mathbf{i}_{\text{ed}} = -A_s \dot{s}_e, \quad (8)$$

135 where ρ_{ed} is the local charge density due to the double-layer capacitance
 136 between the electrode and electrolyte interfaces, and the current density is
 137 represented as

$$\mathbf{i}_{\text{ed}} = -\sigma_{\text{ed}} \nabla \Phi_{\text{ed}}. \quad (9)$$

138 The specific interface area between the electrode and electrolyte is A_s and $\dot{s}_e$
 139 is the net charge-transfer rate associated with the charge-transfer chemistry
 140 (Eq. 3) at the interface,

$$\dot{s}_e = \sum_k z_k F \dot{s}_k. \quad (10)$$

141 The effective electrical conductivity depends on the porosity,

$$\sigma_{\text{ed}} = \sigma_{\text{ed}}^{\circ} (1 - \phi)^{\gamma}, \quad (11)$$

142 where $(1 - \phi)$ is the solid-phase volume fraction, $\sigma_{\text{ed}}^{\circ}$ is the electric conduc-
 143 tivity of dense solid phase, and γ is a Bruggemann exponent.

144 Two boundary conditions are needed to solve Eq. 8. At the cathode
 145 current collector the electrostatic potential is fixed at some reference potential
 146 (typically zero) as

$$\Phi_{\text{ed}} = \Phi_{\text{ref}}. \quad (12)$$

147 At the interface with NASICON, there can be no electric current between
 148 the carbon felt (electrode) and the NASICON. Thus,

$$\mathbf{n} \cdot \mathbf{i}_{\text{ed}} = 0. \quad (13)$$

149 *2.3. Electrolyte charge conservation*

150 The catholyte and the NASICON are both electrolytes and the model
 151 must represent the electrostatic potential distributions within these materi-
 152 als. Although the catholyte and the NASICON are clearly very different, the
 153 same basic charge-conservation equation applies. As illustrated in Fig. 2, it
 154 is convenient in the present model to represent the electrolyte charge con-
 155 servation on a domain that spans NASICON and the catholyte. Of course,
 156 the chemistry and the material properties are greatly different between the
 157 NASICON and the catholyte.

158 The general charge-conservation equation may be represented as

$$\frac{\partial \rho_{\text{el}}}{\partial t} + \nabla \cdot \mathbf{i}_{\text{el}} = A_s \dot{s}_e, \quad (14)$$

159 where ρ_{el} is the local charge density. The electrolyte current density may
 160 be represented in terms of an Ohm's law contribution and a concentration
 161 contribution as

$$\mathbf{i}_{\text{el}} = \sum_k z_k F \mathbf{J}_k = \mathbf{i}_{\text{el,Ohm}} + \mathbf{i}_{\text{el,conc}}. \quad (15)$$

162 The Ohm's law contribution is written as

$$\mathbf{i}_{\text{el,Ohm}} = -\sigma_{\text{el}} \nabla \Phi_{\text{el}}, \quad (16)$$

163 where the conductivity is σ_{el} . Within the catholyte solution, the conductivity
 164 is evaluated from the Nernst–Einstein relationship as

$$\sigma_{\text{el}} = \sum_k \frac{z_k^2 F^2}{RT} D_k^e [X_k], \quad (17)$$

165 where D_k^e are effective diffusion coefficients for the mobile charged species
 166 (Eq. 6) and $[X_k]$ are molar concentrations. In the solid NASICON, the
 167 conductivity is simply the Na^+ conductivity, $\sigma_{\text{el}} = \sigma_{\text{Na}^+}$.

168 Within the catholyte the concentration contribution to the current den-
 169 sity is

$$\mathbf{i}_{\text{el,conc}} = - \sum_k z_k F D_k^e \nabla [X_k]. \quad (18)$$

170 Within the NASICON, the current density is assumed to be purely Ohmic,
 171 meaning that there is no concentration-gradient contribution.

172 Within the catholyte, there is charge transfer between the electrode and
 173 electrolyte phases. The term $\dot{s}_e$ in Eq. 14 is the same as in Eq. 8, but has
 174 the opposite sign. Because there is no charge transfer within the NASICON,
 175 $\dot{s}_e = 0$.

176 The local charge density within the electrolyte phases can be represented
 177 as $\rho_{\text{el}} = \sum z_k F [X_k]$. Except for very fast transients, such as double-layer
 178 charging near electrode interfaces, charge-neutrality within the electrolyte
 179 solutions requires that $\partial \rho_{\text{el}} / \partial t = 0$. The present model neglects these fast
 180 transients, thus considering the steady-state version of Eq. 14.

181 Solving Eq. 14 requires a boundary condition at the interface between
 182 the catholyte and the cathode current collector and a boundary condition
 183 at the interface between the NASICON and the molten sodium (cf., Fig. 2).
 184 At the cathode current collector, the electrical current density must vanish,
 185 $\mathbf{n} \cdot \mathbf{i}_{\text{el}} = 0$. At the molten-sodium interface, the net current current density
 186 must be equal to the current imposed by the external circuit. That is,

$$\mathbf{n} \cdot \mathbf{i}_{\text{el}} = i_{\text{ex}}. \quad (19)$$

187 In principle, Eq. 14 could be solved on the catholyte domain and on the
 188 NASICON domain. In that case, interface conditions would be needed at the
 189 NASICON-catholyte interface. In other words, the electrostatic potential

190 and the charge flux must be continuous across the interface. The present
 191 formulation solves a single discretized equation, but simply changes terms to
 192 represent the materials in the equations on both sides of the interface.

193 **3. Physical and chemical properties**

194 [Table 1 about here.]

195 *3.1. Diffusion coefficients*

196 Mobile-species diffusion coefficients D_k ($\text{m}^2 \text{s}^{-1}$) within the catholyte play
 197 central roles in the battery performance. Temperature-dependent diffusion
 198 coefficients in the dilute aqueous solutions can be formally expressed as [7, 8],

$$D_k(T)\mu(T) = A_k T^{B_k} \exp\left(-\frac{E_k}{RT}\right) \quad (20)$$

199 where μ is the viscosity (Pa s) of the pure water [9], and the parameters
 200 A_k , B_k , and E_k are species-specific parameters. Table 1 lists the diffusivity
 201 parameters used in the present study. The parameters for Na^+ are taken
 202 from Anderko and Lencka [7], considering the relationship of the ionic-species
 203 diffusion coefficients with the limiting conductivities Λ_k° ,

$$\Lambda_k^\circ = \frac{z_k^2 F^2}{RT} D_k. \quad (21)$$

204 The parameters for I_2 and I_3^- are obtained by refitting elevated-temperature
 205 measurements reported by Cantrel, et al. [10]. Parameters for I^- are based
 206 on refitting the experimental data by Cantrel, et al. [11]. Table 1 also shows
 207 the diffusion coefficients evaluated at 25 °C and 120 °C.

208 3.2. NASICON conductivity

209 The present model assumes a NASICON membrane as developed by Ce-
 210 ramatec, Inc. (Salt Lake City, UT). The conductivity for this material σ (S
 211 cm^{-1}) can be represented empirically as [12, 13]

$$\ln(\sigma T) = 11.60996 - \frac{3418.133}{T}, \quad (22)$$

212 where temperature T (in Kelvins) is below 400 °C. At $T = 25$ °C, $\sigma =$
 213 $3.879 \times 10^{-3} \text{ S cm}^{-1}$; at $T = 120$ °C, $\sigma = 4.696 \times 10^{-2} \text{ S cm}^{-1}$.

214 3.3. Carbon felt cathode

215 Carbon felt electrodes can be made by matting, condensing and pressing
 216 carbon fibers. Such materials can have high chemical stability, large specific
 217 surface area, good flow permeability, and high electric conductivity [14]. The
 218 typical porosity ϕ of carbon felt electrodes is around $\phi \approx 0.8$ and the fiber
 219 diameter is typically $d_f \approx 10 \text{ }\mu\text{m}$. The specific area A_s can be expressed
 220 as [15]

$$A_s = \frac{4(1 - \phi)}{d_f}. \quad (23)$$

221 The electric conductivity of the solid matrix σ_{ed} (S m^{-1}) is related to the
 222 porosity ϕ of the carbon-felt porous electrodes as [16]

$$\sigma_{\text{ed}} = 10 + 2800 \left(1 - \frac{\phi}{\phi^\circ}\right)^{1.55}, \quad (24)$$

223 for $0.68 < \phi/\phi^\circ < 1$ where ϕ° is the porosity prior to any mechanical com-
 224 pression. In this study, Eq. 24 is used to estimate the effective electric con-
 225 ductivity of the carbon-felt porous electrode instead of the generic expression
 226 of Eq. 11 for the porous electrode.

227 4. Chemical and electrochemical reactions

228 The Butler–Volmer formulation is used to represent the global charge-
229 transfer rate at electrode-electrolyte interfaces as

$$i_{\text{e,BV}} = i_0 \left[\exp \left(\frac{\alpha_{\text{a}} F \eta_{\text{act}}}{RT} \right) - \exp \left(-\frac{\alpha_{\text{c}} F \eta_{\text{act}}}{RT} \right) \right], \quad (25)$$

230 where the activation overpotential

$$\eta_{\text{act}} = (\Phi_{\text{ed}} - \Phi_{\text{el}}) - E^{\text{eq}} \quad (26)$$

231 and the equilibrium electric potential difference E^{eq} is the electric potential
232 difference at which the forward and backward charge-transfer rates are equal
233 to the exchange current density i_0 . α_{a} and α_{c} are the anodic and cathodic
234 symmetric factors, respectively.

235 4.1. Na^+/Na charge transfer kinetics

236 The reversible half-cell potential of the electrochemical reaction (Eq. 2)
237 at the metallic sodium-NASICON interfaces can be expressed as

$$E_{\text{Na}^+}^{\text{eq}} = E_{\text{Na}^+}^{\circ} + \frac{RT}{F} \ln a_{\text{Na}^+}, \quad (27)$$

238 The activity of sodium ion is defined as $a_{\text{Na}^+} = \gamma_{\text{Na}^+} [\text{Na}^+] / [\text{Na}^+]^{\circ}$ where the
239 activity coefficient γ_{Na^+} is assumed to be 1, and the concentration of sodium
240 ion at the standard state $[\text{Na}^+]^{\circ}$ is equal to 1 M. The standard reduction
241 potential $E_{\text{Na}^+}^{\circ} = -2.714$ V with respect to the standard hydrogen electrode.
242 The exchange current density can be expressed as

$$i_0 = i_0^{\circ} \left(\frac{[\text{Na}^+]}{[\text{Na}^+]^*} \right)^{\alpha_{\text{a}}}. \quad (28)$$

243 where i_0° is an empirical fitting parameter for the exchange current density,
 244 and the reference concentrations of $[\text{Na}^+]^*$ is taken to be 1 M. Because the
 245 Butler-Volmer equation represents the net charge-transfer rates rather than
 246 the elementary mass-action kinetics [17, 18], the exponent for the sodium-ion
 247 concentration $[\text{Na}^+]$ is usually different from the stoichiometric coefficient of
 248 the charge-transfer reaction.

249 4.2. Iodine redistribution chemistry

250 Although iodine (I_2) is soluble in a sodium iodide aqueous solution,
 251 the equilibrium iodine concentration is relatively small compared to iodide
 252 and tri-iodide concentrations. Assuming that iodine precipitation is to be
 253 avoided, the redox process largely occurs between the iodine and tri-iodide
 254 couple within the catholyte solution. The $\text{I}^-/\text{I}_3^-/\text{I}_2$ redox processes have
 255 been widely investigated in conventional (i.e., water, acetonitrile, DMSO)
 256 and ionic-liquid solvents for dye-sensitized solar cells [19–22].

257 The redox chemistry for the iodide/iodine (I^-/I_2) couple on the surface of
 258 inert electrodes (e.g., platinum or carbon) can be expressed globally as Re-
 259 action 3. However, based on measurements by Wroblowa and Saunders [23],
 260 a two-step process provides a better physical representation as

261

262 where $\text{I}(\text{s})$ is the adsorbed iodine on the electrode surface, and (s) is the
 263 unoccupied or empty site on the electrode surface. The present model builds
 264 on this two-step cathode chemistry.

265 Assuming Reaction 30 to be the rate-limiting step, the equilibrium of
 266 Reaction 29 can be represented as

$$\frac{\theta_I}{\theta_v} = (K_{29}[\text{I}_2])^{1/2}, \quad (31)$$

267 where θ_I and θ_v are the site fractions of I(s) and (s) on the electrode surface
 268 and K_{29} is the equilibrium constant. Assuming $\theta_I + \theta_v = 1$, θ_I and θ_v can be
 269 evaluated as

$$\theta_v = \frac{1}{1 + (K_{29}[\text{I}_2])^{1/2}}, \quad (32)$$

$$\theta_I = \frac{(K_{29}[\text{I}_2])^{1/2}}{1 + (K_{29}[\text{I}_2])^{1/2}}. \quad (33)$$

271 The current density resulting from the rate-limiting charge-transfer process
 272 (Eq. 30) can be represented in elementary (Marcus) form as

$$i_e = k_{30,f} \exp\left(\frac{\beta_a FE}{RT}\right) [\text{I}^-] \Gamma \theta_v - k_{30,b} \exp\left(-\frac{\beta_c FE}{RT}\right) \Gamma \theta_I, \quad (34)$$

273 where E is the electrostatic-potential difference between electrode and elec-
 274 trolyte phases and Γ is the available site density. The anodic and cathodic
 275 symmetric factors are β_a and β_c , with $\beta_a + \beta_c = 1$ for an elementary (single-
 276 electron transfer) reaction. $k_{30,f}$ and $k_{30,b}$ are the forward and backward
 277 rate coefficients of Reaction 30. Representing the current density in Butler-
 278 Volmer form, the exchange current density i_0 as functions of iodine and iodide
 279 concentrations can be expressed as

$$i_0 = i_0^\circ \frac{([\text{I}_2]/[\text{I}_2]^*)^{\beta_a/2} ([\text{I}^-]/[\text{I}^-]^*)^{1-\beta_a}}{1 + ([\text{I}_2]/[\text{I}_2]^*)^{1/2}}, \quad (35)$$

280 where the reference iodine concentration $[\text{I}_2]^* = K_{29}^{-1}$, which is considered to
 281 be much larger than $[\text{I}_2]$ such that $\theta_I \ll 1$ and $\theta_v \approx 1$ [23]. The reference io-
 282 dide concentration $[\text{I}^-]^*$ is taken as 1 M. The equilibrium reversible potential

283 $E_{\text{I}^-/\text{I}_2}^{\text{eq}}$ can be expressed as

$$E_{\text{I}^-/\text{I}_2}^{\text{eq}} = E_{\text{I}^-/\text{I}_2}^{\circ} + \frac{RT}{2F} \ln \frac{a_{\text{I}_2}}{a_{\text{I}^-}^2}, \quad (36)$$

284 The activity for I_2 is defined as $a_{\text{I}_2} = \gamma_{\text{I}_2}[\text{I}_2]/[\text{I}_2]^{\circ}$, and the activity for I^-
 285 is $a_{\text{I}^-} = \gamma_{\text{I}^-}[\text{I}^-]/[\text{I}^-]^{\circ}$. The activity coefficients γ_{I_2} and γ_{I^-} are assumed to
 286 be 1, and the concentrations at the standard state $[\text{I}_2]^{\circ}$ and $[\text{I}^-]^{\circ}$ are equal
 287 to 1 M. The redox potential of iodine/iodide couple at the standard state is
 288 $E_{\text{I}^-/\text{I}_2}^{\circ} = 0.5335$ V with respect to the hydrogen standard electrode.

289 The iodide and iodine can combine homogeneously to form the complex
 290 polyhalogen tri-iodide anion,

291 where the forward rate coefficient $k_{37,\text{f}}$ and backward rate coefficient $k_{37,\text{b}}$ are
 292 related to the equilibrium constant K_{37} in the usual way as $K_{37} = k_{37,\text{f}}/k_{37,\text{b}}$.
 293 Because of the formation of the intermediate tri-iodide, the processes of the
 294 iodide oxidation and iodine reduction may proceed phenomenally or appar-
 295 ently in two steps as

296

297 which may lead to two observable voltammetric processes or waves. The
 298 potential gap of the two voltammetric waves is proportional to the magnitude
 299 of equilibrium constant of the tri-iodide formation reaction K_{37} .

300 4.3. Boiling temperature of aqueous NaI solution

301 Briggs and Geigle [24] reported the boiling temperatures of the aqueous
 302 sodium iodide solution as function of the weight percentage of sodium iodide
 303 in water at about 0.98 atmospheric pressure as shown in Fig. 3. As illustrated
 304 in Fig. 3, the boiling temperature increases as more sodium iodide is added
 305 into the water. The boiling temperature is about 120 °C at the NaI weight
 306 percentage of 64% with the corresponding molar concentration of NaI of
 307 about 8 M. At the saturation point where the NaI weight percentage is about
 308 76% and the NaI molar concentration is about 11 M, the boiling temperature
 309 can reach to about 142 °C. In this study, the operating temperature of the
 310 battery is chosen to be 120 °C, which is above the melting temperature of
 311 metal sodium within the anode (97.79 °C), and below the boiling temperature
 312 of aqueous NaI solution with appropriate NaI concentrations.

313 [Figure 3 about here.]

314 4.4. Equilibrium constant of tri-iodide formation

315 The reaction equilibrium constant of the tri-iodide formation K_{37} depends
 316 highly on the solvents [25]. For the aqueous solutions, the enthalpy and
 317 entropy changes at 25 °C are $\Delta H_{37}^\circ = -17.0 \text{ kJ mol}^{-1}$, $\Delta S_{37}^\circ = -0.6 \text{ J K}^{-1}$
 318 mol^{-1} respectively, and $K_{37} \approx 700$ at 25 °C [26]. The equilibrium constant
 319 K_{37} at high temperature has been widely investigated [26–28] and can be
 320 represented empirically as [26, 29]

$$\log K_{37} = 555.0/T + 7.355 - 2.575 \log T, \quad (40)$$

321 where T is in Kelvins and K_{37} has molarity units as M^{-1} . Guo, et al. [30] have
 322 compared several alternative temperature-dependent correlations for K_{37} .

323 The equilibrium molar concentrations of I^- , I_2 and I_3^- within the aque-
 324 ous catholyte solution at a given iodine element concentration $[\text{I}]$, sodium
 325 ion concentration $[\text{Na}^+]$, and temperature can be evaluated based on the
 326 equilibrium relationship

$$\frac{[\text{I}_3^-]}{[\text{I}^-][\text{I}_2]} = K_{37}, \quad (41)$$

327 together with the element balance

$$[\text{I}^-] + 2[\text{I}_2] + 3[\text{I}_3^-] = [\text{I}], \quad (42)$$

328 and charge balance

$$[\text{I}^-] + [\text{I}_3^-] = [\text{Na}^+]. \quad (43)$$

329 Considering $[\text{I}] = 8.0 \text{ M}$ and $[\text{Na}^+] = 3.81 \text{ M}$ at $T = 25 \text{ }^\circ\text{C}$, the equilibrium
 330 concentrations are 1.716 M for $[\text{I}^-]$, 2.09 M for $[\text{I}_3^-]$ and $1.74 \times 10^{-3} \text{ M}$ for
 331 $[\text{I}_2]$, which indicates that the equilibrium iodine molar concentration is much
 332 smaller than the equilibrium iodide and tri-iodide molar concentrations.

333 5. Solubility and state of charge

334 The solubility of sodium iodide in pure water at $25 \text{ }^\circ\text{C}$ is 184.2 g per 100
 335 g of water, at which point the solution density is $1.9169 \times 10^3 \text{ kg m}^{-3}$ [31].
 336 Consequently, the saturated NaI concentration is $[\text{NaI}]_{\text{max}} \approx 8.286 \text{ M}$. Upon
 337 the full discharge of Na-I_2 batteries, all the iodine is oxidized to NaI . Be-
 338 cause the total iodine element concentration $[\text{I}]$ remains constant within the
 339 catholyte solution, precipitation of sodium iodine can be avoided as long as
 340 $[\text{I}] \leq [\text{NaI}]_{\text{max}}$ under fully discharged conditions. The solubility of sodium
 341 iodide in pure water increases as the temperature increases. At $100 \text{ }^\circ\text{C}$, 302
 342 g of sodium iodide can dissolve into 100 g of water; at $120 \text{ }^\circ\text{C}$ 310 g of sodium

iodide can dissolve into 100 g of water [32]. The saturated molar concentration of sodium iodide is $[\text{NaI}]_{\text{max}} \approx 11.1 \text{ M}$ at 100 °C and $[\text{NaI}]_{\text{max}} \approx 11.2 \text{ M}$ at 120 °C.

Iodine (I_2) is a bluish-black solid below its melting temperature of 113.5 °C. It volatilizes into a blue-violet gas with an irritating odor at the room temperature. Iodine is slightly soluble in water and becomes more soluble as the temperature increases. The water solubility of iodine is 0.34 g per liter at 25 °C, then increases to 0.78 g per liter at 50 °C. Iodine is more soluble in sodium-iodide solutions because of formation of tri-iodide through combination of iodine with iodide. At 25 °C, the iodine solubility is related to the sodium-iodide molar concentration in water as [33]

$$[\text{I}_2] \approx 0.55[\text{NaI}]. \quad (44)$$

Therefore, for a specified iodine element concentration $[\text{I}]$, the sodium ion concentration $[\text{Na}^+]$ must be greater than about $0.47619[\text{I}]$, such that precipitation of iodine can be avoided during charging the Na- I_2 batteries (i.e., $[\text{Na}^+]_{\text{min}} = 0.47619[\text{I}]$).

Table 2 lists fully charged and discharged species molar concentrations within the catholyte at four iodine element concentrations: 4.0, 6.0, 8.0 and 10.0 M. The sodium iodine concentration is set to be below the solubility limit to avoid NaI precipitation at the fully discharged state, and to be high enough to avoid I_2 precipitation at the fully charged state. During the charging and discharging processes, the species molar concentrations vary spatially through the cathode. It is important to monitor the local variation of the species molar concentrations such that $[\text{Na}^+] \leq [\text{NaI}]_{\text{max}}$ and $[\text{Na}^+]/[\text{I}] \geq 0.476$ to avoid any local precipitation of NaI and I_2 through the cathode.

367 The state of charge (SOC) as a relative measure of the amount of energy
 368 storage in the Na-I₂ battery can be defined based on the species concentra-
 369 tions within the catholyte solution. Because the practical cell capacity seeks
 370 to remain within the precipitation limits, the sodium ion concentration dur-
 371 ing the charge and discharge processes should be maintained in the range of
 372 $0.47619[\text{I}] \leq [\text{Na}^+] \leq [\text{I}]$ at a specified iodine element concentration $[\text{I}]$. The
 373 state of charge for the Na-I₂ battery may be defined as

$$\text{SOC} = \frac{[\text{I}] - \overline{[\text{Na}^+]}}{[\text{I}] - [\text{Na}^+]_{\min}}, \quad (45)$$

374 which varies from zero in the fully discharged state to unity in the fully
 375 charged state. The average molar concentrations within the catholyte $\overline{[X_k]}$
 376 are defined as

$$\overline{[X_k]} = \frac{1}{L_c} \int_0^{L_c} [X_k] dx, \quad (46)$$

377 where L_c is the thickness of the catholyte.

378 [Table 2 about here.]

379 6. Discretization and software implementation

380 The solution algorithm generally follows the method-of-lines [34, 35]. The
 381 spatial operators in Eqs. 4 and 14 are discretized using a conservative finite-
 382 volume formulation. After the spatial operators of the partial differential
 383 equations are discretized, the resulting system forms a system of ordinary
 384 differential-algebraic equations (DAE). The DAEs are solved using the LIMEX
 385 software [36]. The numerical algorithm is implemented in Fortran, using
 386 electrochemical extensions of the CHEMKIN software [35]. Because CHEMKIN

387 package was written initially for gas-phase chemistry, new functionality was
388 added to handle the thermodynamics of liquid electrolyte solutions.

389 7. Results and discussion

390 A nominal battery architecture and operating conditions are used to illus-
391 trate the model and explore salient aspects of model-predicted performance.
392 Table 3 summarizes some of the geometric and chemical parameters. Table 1
393 lists transport parameters. Both the molten-sodium anode and the porous
394 cathode structure are 10 mm thick and the NASICON separator is 200 μm
395 thick. The cell operating temperature is assumed to be 120 $^{\circ}\text{C}$. The nominal
396 conductivity of the carbon felt is $\sigma_{\text{ed}} = 100 \text{ S m}^{-1}$. The nominal charge and
397 discharge rates are assumed to be 1C. The current density at 1 C is about
398 90 mA cm^{-2} .

399 The model predicts spatial profiles of species concentration and electrostatic-
400 potential. The overall cell performance is characterized in terms of the cell
401 voltage, state of charge, and solubility limits. Following discussion of the
402 nominal performance, physical parameters and operating conditions are var-
403 ied to study their influences on performance. These studies consider the
404 effects of charge/discharge rates, total elemental iodine concentration, and
405 electrical conductivity of the porous carbon-felt cathode.

406 [Table 3 about here.]

407 [Figure 4 about here.]

408 7.1. Charge and discharge characterization

409 [Figure 5 about here.]

410 Under the nominal conditions, Fig. 4 shows the cell voltages as functions
 411 of the state of charge (SOC) and time during the first charge and discharge
 412 cycles. The initial species concentrations within the catholyte are assumed to
 413 be spatially uniform in the fully discharged state (Table 2, $[I] = 8 \text{ M}$) and the
 414 charge and discharge rates are set to be 1 C. The solid lines of Fig. 4 shows
 415 that the cell is charged from the fully discharged state (i.e., $\text{SOC} = 0.0$). At
 416 the charging rate of 1C, the cell voltage E_{cell} is about 3.05 V at $\text{SOC} = 0.0$,
 417 and increases continuously to about 3.19 V at $\text{SOC} \approx 0.5$, and finally reaches
 418 to 3.26 V at $\text{SOC} \approx 0.94$ because the sodium-ion concentration approaches
 419 $[\text{Na}^+]/[I] = 0.476$. Immediately upon achieving the maximum charged state,
 420 a 1C discharge is initiated. Reversing the current density to the discharge
 421 mode causes the cell voltage to drop to approximately 3.03 V. The battery
 422 continues to discharge at 1C until a lower-limit SOC is achieved where NaI
 423 would begin to precipitate. At this nearly discharged point, the cell voltage
 424 is $E_{\text{cell}} = 2.82 \text{ V}$. As represented by the solid lines in Fig. 4, the second 1C
 425 charge cycle begins immediately upon reaching the first discharge limit. The
 426 process can continue in a limit cycle for many charge-discharge cycles. If the
 427 charge/discharge rates were lower, the battery could achieve its equilibrium
 428 fully charged and discharged states. At high rates, the envelope of the limit
 429 cycle would shrink.

430 [Figure 6 about here.]

431 7.1.1. Charging, $\text{SOC}=0.5$

432 Figure 5 shows solution profiles at $\text{SOC}=0.5$ of the first charge cycle
 433 (“star” on Fig. 4). By this point in the charge, significant spatial variation

434 is evident in all the profiles. During charging, Na^+ is being transported
 435 from the cathode toward the NASICON and the anode. The gradients of
 436 both the Na^+ and the electrolyte electrostatic potential Φ_{el} are positive.
 437 Thus the concentration and migration contributions in the Nernst–Planck
 438 flux (cf., Eq. 5) are in the direction of driving Na^+ toward the NASICON.
 439 During charging, the cathode charge-transfer reaction (Eq. 3) is proceeding
 440 in the anodic direction (i.e., producing electrons and iodine). Thus, the I_2
 441 concentration is high near the cathode current collector. To balance charge,
 442 the concentrations of the two anions (I^- and I_3^-) are highest where the cation
 443 (Na^+) concentration is highest. Additionally, there is a coupled redistribution
 444 of the elemental iodine according to Eq. 37. The concentration of I_2 is always
 445 much smaller than the other concentrations. If $[\text{I}_2]$ becomes too large, then
 446 it cannot remain in solution and deleterious precipitation will occur.

447 Figure 5b shows profiles of the total elemental iodine concentration $[\text{I}]$ and
 448 the ratio $[\text{Na}^+]/[\text{I}]$. Because iodine cannot leave the cathode compartment,
 449 the total $[\text{I}]$ level within the catholyte remains fixed. In this example, it is
 450 fixed at $[\text{I}] = 8 \text{ M}$. Although the total elemental iodine is fixed, the spatial
 451 profiles of all the iodine-contains species can vary greatly. The ratio $[\text{Na}^+]/[\text{I}]$
 452 is important because it indicates the propensity for precipitation. During
 453 charging (with $[\text{I}] = 8 \text{ M}$), the sodium concentration within the catholyte
 454 must be maintained as $[\text{Na}^+]/[\text{I}] > 0.476$. As shown in Fig. 5b, $[\text{Na}^+]/[\text{I}]$ has
 455 a local maximum in the interior of the cathode chamber, but is lowest in the
 456 vicinity of the cathode current collector.

457 Figure 5c shows spatial profiles of the exchange current density, Butler–
 458 Volmer charge-transfer rate, and the activation overpotential associated with

Reaction 3. The overpotential η_c is highest near the cathode current collector, where the local charge-transfer rate $i_{\text{BV,e}}$ is also the highest. As is evident from Eq. 35, the exchange current density i_0 (Eq. 25) has a complicated dependence on the species concentrations.

Figure 5d shows profiles of the equilibrium electric-potential difference ($E_{\text{I}^-/\text{I}_2}^{\text{eq}} = (\Phi_{\text{ed}} - \Phi_{\text{el}})^{\text{eq}}$), as well as the local electrostatic potentials of the electrode Φ_{ed} (Carbon felt) and electrolyte Φ_{el} (catholyte solution). Note that $E_{\text{I}^-/\text{I}_2}^{\text{eq}}$ is positive (the negative is plotted), whereas both the electrostatic potentials are negative. The electrostatic-potential difference ($E = \Phi_{\text{ed}} - \Phi_{\text{el}}$) is approximately $E = 0.5$ V. Thus, during charging, the cathode's activation overpotential η_c (Eq. 26) has small positive values, as shown in Fig. 5c.

Throughout the charging processes, current is driven from the cathode current collector toward the NASICON membrane. Electronic current from the cathode current collector is transported throughout the porous electrode and is continuously converted into the ionic current within the catholyte solution by the charge-transfer reactions. Consequently, the electronic current density within the porous electrode decreases and ionic current density within the catholyte solution increases as net current travels from the cathode current collector to the NASICON membrane. The electrode electrostatic potential gradient $\nabla\Phi_{\text{ed}}$ decreases and electrolyte electrostatic potential gradient $\nabla\Phi_{\text{el}}$ increases as a function of position between the NASICON and the cathode current collector (Fig. 5d).

7.1.2. Charging, SOC=0.94

Figure 6 shows the spatial profiles in the same format as Fig. 5, but near the end of the 1C charge cycle. Qualitatively, the profiles have similar shapes.

484 However, the $[\text{Na}^+]/[\text{I}]$ profiles is important. At SOC=0.94, near the cathode
 485 current collector $[\text{Na}^+]/[\text{I}]$ is approaching the I_2 solubility limit. Thus, to
 486 avoid precipitation, the 1C charging is terminated before achieving full state
 487 of charge. Even in this state, the charging could continue to proceed, but at
 488 a lower rate.

489 If the 1C charging process was simply terminated at SOC=0.94 and the
 490 battery was left at rest, then all the profiles would relax toward uniform
 491 distribution. The state of charge would remain at SOC=0.94, but $[\text{Na}^+]/[\text{I}]$
 492 would increase away from the precipitation limit. The charging process could
 493 resume without precipitation.

494 7.1.3. *Electrostatic potential differences*

495 The net electrostatic-potential differences across the cathode compart-
 496 ment for the electronic-conducting phase $\Delta\Phi_{\text{ed}}$ and ionic-conducting phase
 497 $\Delta\Phi_{\text{el}}$ can be defined as the absolute value of the differences between the
 498 electrostatic potentials at the current-collector interface and the NASICON
 499 interface. At SOC = 0.5 (Fig. 5), $\Delta\Phi_{\text{ed}} = 0.0351$ V and $\Delta\Phi_{\text{el}} = 0.0365$ V.
 500 At SOC=0.94 (Fig. 6), $\Delta\Phi_{\text{ed}} = 0.0357$ V and $\Delta\Phi_{\text{el}} = 0.0639$ V. $\Delta\Phi_{\text{ed}}$ in
 501 this case is essentially independent of the state-of-charge. However, as the
 502 battery charges, the ion concentrations within the catholyte decrease. As
 503 a result, based on the Nernst–Einstein relationship (Eq. 17), the electrolyte
 504 conductivity decreases. Thus, the polarization associated with ion trans-
 505 port increases as the battery charges. At SOC=0.94 $\Delta\Phi_{\text{el}}$ is nearly double
 506 what it is at SOC=0.5. Comparing Figs. 5c and 6c, at high SOC the local
 507 charge-transfer rates (i.e., $i_{\text{BV,e}}$) are somewhat higher near the cathode cur-
 508 rent collector and lower near the NASICON. Of course, at fixed charge rate

509 (i.e., 1C), the net charge-transfer rate (i.e., the integral of $i_{\text{BV},e}$) must be the
 510 same independent of SOC. As discussed subsequently, the variations in $\Delta\Phi_{\text{el}}$
 511 play a more prominent role at higher charge and discharge rates.

512 [Figure 7 about here.]

513 [Figure 8 about here.]

514 7.1.4. Discharging

515 The dashed lines on Fig. 4 show cell voltage as a function of SOC and time
 516 for a cell that was initially fully charged with spatially uniform profiles (i.e.,
 517 SOC = 1.0, $E_{\text{cell}} = 3.05$ V). Discharging at 1C, the cell voltage decreases
 518 continuously to about 2.99 V at SOC=0.5. The discharge terminates at
 519 SOC=0.025 where the cell voltage is approximately 2.89 V. The 1C discharge
 520 is terminated because the Na^+ concentration increases to the point that
 521 NaI precipitation would be initiated. Assuming that 1C charging begins
 522 immediately upon terminating the 1C discharge, the cell voltage immediately
 523 increases to $E_{\text{cell}} = 3.09$ V. The subsequent 1C charging follows very closely
 524 the charging curve that resulted from an initially fully discharged state.

525 Fig. 7 shows spatial profiles at SOC ≈ 0.5 during the 1C discharge.
 526 Comparing Figs. 5 and 7, it is evident that the profiles are qualitatively
 527 different between charging and discharging. During discharge, Na^+ enters
 528 the catholyte from the NASICON, causing negative gradients for the Na^+
 529 concentration. Electrons enter from the cathode current collector and are
 530 conducted through carbon felt. To maintain charge neutrality, the anion
 531 ($[\text{I}^-]$ and $[\text{I}_3^-]$) concentration gradients are also negative. The gradients of

the total iodine $[I]$ as well as the $[Na^+]/[I]$ are opposite to those in the charging process. Referring to Fig. 7c, note that the activation overpotentials and Butler–Volmer charge-transfer rates are both negative. A negative charge-transfer rate means that Reaction 3 is proceeding in the cathodic direction (i.e., consuming electrons). The electrostatic potentials Φ_{ed} and Φ_{el} both decrease from the NASICON interface toward the cathode current collector.

Figure 8 shows profiles during discharge, but at the near fully discharged state. The discharge is terminated at SOC=0.025 to avoid precipitation. Comparing Figs. 7 and 8, it is evident that the profiles are qualitatively similar. Comparing Figs. 7d and 8d, it can be seen that the electrolyte electrostatic potentials Φ_{el} are different by approximately 100 mV between SOC=0.5 and SOC=0.025. At SOC=0.025 the Na^+ concentrations are high in the fully discharged state, causing the electrolyte conductivity to be high (Eq. 17). This, in turn, causes the catholyte electrostatic-potential gradients to be lower than that in the partially discharged state. In the fully discharged state the Na^+ is charge-balanced primarily by I^- , with very low concentrations of I_3^- .

Referring to Fig. 7, at SOC=0.5, $\Delta\Phi_{ed} = 0.0401$ V and $\Delta\Phi_{el} = 0.0283$ V. Referring to Fig. 8, SOC=0.025, $\Delta\Phi_{ed} = 0.0669$ V and $\Delta\Phi_{el} = 0.0093$ V. The charge-transfer process tends to be located in the regions nearer to the NASICON. At low SOC the electrons need to travel further through the carbon felt, causing $\Delta\Phi_{ed}$ to be larger at low SOC. However, $\Delta\Phi_{el}$ is relatively low at SOC=0.025, which is caused by the high electrolyte conductivity and thus relatively low polarization associated with ionic current.

556 *7.2. Effects of charge/discharge rates*

557 [Figure 9 about here.]

558 Continuing to consider the nominal battery layout and operating con-
 559 ditions, Fig. 9 illustrates the effects of the charge rate (0.5C, 1.0C, 2.5C,
 560 and 5.0C). The current density is 44.9 mA cm⁻² for 0.5C, 89.8 mA cm⁻²
 561 for 1.0C, 224.6 mA cm⁻² for 2.5C, and 449.2 mA cm⁻² for 5.0C. The cell
 562 is initially set to be at the fully discharged state with the uniform species
 563 concentrations (Table 2). Figure 9a shows the cell voltage increases as the
 564 charge rate increases. To prevent precipitation, maximum achievable state of
 565 charge SOC_{max} decreases significantly as the charging rate increases. More-
 566 over, the time required to achieve the maximum SOC decreases as the charge
 567 rate increases. At 1C, achieving SOC_{max} ≈ 0.94 takes approximately 3384
 568 s. At 5C, achieving SOC_{max} ≈ 0.47 takes approximately 338 s. Table 4
 569 summarizes the SOC_{max} and time to achieve maximum charge as functions
 570 of charge rate.

571 Figure 9b shows $\Delta\Phi_{\text{ed}}$ and $\Delta\Phi_{\text{el}}$ as functions of SOC for different charge
 572 rates. The electrostatic-potential difference within the electron-conducting
 573 phase $\Delta\Phi_{\text{ed}}$ is highest at high charge rates, but is only weakly affected by the
 574 state of charge. By contrast, $\Delta\Phi_{\text{el}}$ depends strongly on the charge rate and
 575 the state of charge. At the relatively low charge rates (0.5C and 1C) $\Delta\Phi_{\text{el}}$
 576 increases almost linearly as functions of the state of charge. At the relatively
 577 high charge rates (2.5C and 5C), $\Delta\Phi_{\text{el}}$ increases rapidly in the approach
 578 to the maximum state of charge. At the high charge rates, the low Na⁺
 579 diffusivity and concentration gradient limits the mobility of Na⁺ transport
 580 toward the NASICON membrane. Consequently, very large electrostatic-

581 potential gradients $\nabla\Phi_{\text{el}}$ are required to increase the ion-migration flux (cf.,
 582 Eq. 5) to satisfy the imposed charge rate, which leads to rapid increase of
 583 $\Delta\Phi_{\text{el}}$, and also E_{cell} .

584 [Table 4 about here.]

585 [Figure 10 about here.]

586 Figure 10 is comparable to Fig. 9, but for the discharge process. The
 587 cell is assumed to be initially at the fully charged state with uniform equilib-
 588 rium species molar concentrations (Table 2). As was the case with charging,
 589 cell voltages and electrostatic potentials depend strongly on the discharge
 590 rates. Figure 10a shows that the cell voltages decrease by about 0.5 V as
 591 the discharge rate increases from 0.5C to 5C. The minimum achievable state
 592 of charge SOC_{min} increases greatly as the discharge rate increases. At 0.5C,
 593 the cell can be essentially fully discharged. However, SOC_{min} increases to
 594 approximately 0.68 at 5C. Table 4 summarizes SOC_{min} and discharge time
 595 to reach SOC_{min} for different discharge rates.

596 Figure 10b shows that both $\Delta\Phi_{\text{ed}}$ and $\Delta\Phi_{\text{el}}$ increase as the discharge
 597 rate increases. For each discharge rate, $\Delta\Phi_{\text{el}}$ continuously decreases as the
 598 cell becomes more discharged. The gradient $\nabla\Phi_{\text{el}}$ increases at the high dis-
 599 charge rates. At the high discharge rates the high Na^+ flux that enters the
 600 catholyte solution from the NASICON leads to large species concentration
 601 gradients near the NASICON membrane. Because of transport limitations,
 602 ionic species concentrations are relatively high near the NASICON, lead-
 603 ing to relatively high local electrolyte conductivities. As a consequence, the
 604 magnitudes of the gradients $\nabla\Phi_{\text{el}}$ remain relatively low. Nevertheless, the

solubility limit of NaI near the NASICON limits the discharge. Figure 10b shows that $\Delta\Phi_{\text{ed}}$ slightly increases as SOC decreases due to the shift of local charge-transfer rate toward the region near the NASICON. The steep asymptotic behavior that is evident in high-rate charging (Fig. 9) is not present in as the discharge reaches the limits.

7.3. *Effect of catholyte concentrations*

The total elemental iodine loading greatly affects the ion concentrations and the solubility limits (Table 2). Figure 11 shows how the iodine loading affects the charge process. In all cases shown the charge rate is fixed at $i_{\text{ex}} = 100 \text{ mA cm}^{-2}$ and the operating temperature is 120°C . The charging process begins from the equilibrium fully discharged condition.

[Table 5 about here.]

As the elemental iodine loading increases, the ion concentrations within the catholyte solution increase, leading to higher electrolyte conductivity (Eq. 17). As a result $\Delta\Phi_{\text{el}}$ decreases at high iodine loadings. Thus, lower cell potentials E_{cell} required to charge the battery with higher iodine (Fig. 11a). Figure 11a also shows that SOC_{max} is about 0.74 at $[\text{I}] = 4 \text{ M}$, and increases to about 0.94 at $[\text{I}] = 8.0 \text{ M}$. Table 5 summarizes SOC_{max} and the required charging times.

[Figure 11 about here.]

[Figure 12 about here.]

Figure 12 shows discharge characteristics as functions of SOC for the four elemental iodine concentrations. As the iodine loading increases, the electrostatic-potential differences $\Delta\Phi_{\text{ed}}$ and $\Delta\Phi_{\text{el}}$ increase by less than 0.1 V. As a result E_{cell} decreases only very slightly as the iodine loading increases. However, SOC_{min} increases significantly from the being able to fully discharge at $[\text{I}] = 4.0 \text{ M}$ to about 0.37 at $[\text{I}] = 10.0 \text{ M}$. Table 5 summarizes the SOC_{min} and the discharge times as functions of the iodine loading.

7.4. *Effect of cathode conductivity*

The conductivity of porous electrode felt depends on the porosity and the mechanical compression (Eq. 24). The electrode conductivity can vary from 10 S m^{-1} at no mechanical compression to about 500 S m^{-1} at large mechanical compression. Considering four electrode conductivities and a charge rate of 1C, Fig. 13 shows cell voltages and electrostatic-potential differences as functions of SOC during charging. In all cases, the porosity is fixed as $\phi = 0.8$. As the electrode conductivity decreases, the resistance for the electron transport through the porous cathode felt increases, causing $\Delta\Phi_{\text{ed}}$ to increase (Fig. 13b). The charge-transfer processes are localized near the cathode current collector, which leads to the increases of $\Delta\Phi_{\text{el}}$ as the ion flux needs must travel further to reach the NASICON. The high concentration of I_2 at the interface with the cathode current collector limits the maximum achievable state of charge. With $\sigma_{\text{ed}} = 10 \text{ S m}^{-1}$, $\text{SOC}_{\text{max}} \approx 0.54$ (Fig. 13a). At the nominal $\sigma_{\text{ed}} = 100 \text{ S m}^{-1}$, $\text{SOC}_{\text{max}} \approx 0.94$.

[Figure 13 about here.]

[Figure 14 about here.]

Figure 14 shows cell potentials during 1C discharge, with four different electrode conductivities. Decreasing cathode conductivity leads to increased polarization and lower cell voltages. At full charge the cell voltage is $E_{\text{cell}} \approx 3.06$ V when $\sigma_{\text{ed}} = 200$ S m⁻¹, but is reduced to about 2.96 V when $\sigma_{\text{ed}} = 10$ S m⁻¹. The very low electrode conductivity of 10 S m⁻¹ is actually smaller than the electrolyte conductivity. Under this assumption the charge-transfer processes within the cathode moves closer to the cathode current collector such that the electronic current travels shorter distance to reach the current collector. As I_3^- and I_2 in the region near to the cathode current collector are fully discharged into I^- , the charge-transfer processes move away from the current collector and the electronic current must travel further to reach the cathode current collector. This, in turn, causes $\Delta\Phi_{\text{ed}}$ to increase (Fig. 14b) and large decreases in cell voltage (Fig. 14a). Low electrode conductivity also leads to early termination of the discharge processes. Assuming $\sigma_{\text{ed}} = 10$ S m⁻¹, $\text{SOC}_{\text{min}} \approx 0.57$.

8. Summary and conclusions

A new computational model is derived and applied to predict performance of a Na-I₂ rechargeable battery. A molten-sodium anode is separated by a NASICON membrane from a porous-carbon cathode that is infiltrated with an aqueous catholyte. The NASICON is a pure Na-ion conductor. Using a Nernst–Planck formulation, the model considers the transport of four mobile species (Na^+ , I^- , I_3^- and I_2) within the catholyte. A Butler–Volmer formulation is used to represent the charge-transfer chemistry at the interface between the molten sodium and the NASICON and at the interfaces

674 between the porous-carbon cathode and the catholyte solution. Overall,
 675 the chemistry can be represented as $2\text{Na}^+ + 2\text{I}^- \rightleftharpoons 2\text{Na} + \text{I}_2$. However, the
 676 cathode chemistry is more complex, including iodine redistribution between
 677 I^- , I_3^- and I_2 . The model considers the solubility of NaI and I_2 within the
 678 catholyte. Depending on the charge or discharge rate, catholyte solubility
 679 limits the state-of-charge that can be achieved. The model predicts the effects
 680 of charge/discharge rates, iodine concentrations, and electrode conductivities
 681 on battery performance.

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690 10. References

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Table 1: Parameters for diffusion coefficients in a dilute aqueous solution and diffusion coefficients evaluated at $T = 25\text{ }^{\circ}\text{C}$ and $T = 120\text{ }^{\circ}\text{C}$

Ion	A	B	E (kJ mol ⁻¹)	D (25°C) (10 ⁻⁵ cm ² s ⁻¹)	D (120°C)
Na ⁺	3.1040×10^{-15}	+1	-0.628	1.3434	6.3867
I ⁻	2.4952×10^{-15}	+1	-2.020	1.8941	7.8625
I ₂	2.3721×10^{-15}	+1	-1.302	1.3475	5.9989
I ₃ ⁻	2.5238×10^{-15}	+1	-0.674	1.1130	5.2677

Table 2: Equilibrium molar concentrations under fully discharged and fully charged conditions, with different total elemental iodine concentrations.

Total iodine	Fully discharged			
[I] (M)	[Na ⁺] ₀ (M)	[I ⁻] ₀ (M)	[I ₃ ⁻] ₀ (M)	[I ₂] ₀ (M)
4.0	4.0	4.0	0.0	0.0
6.0	6.0	6.0	0.0	0.0
8.0	8.0	8.0	0.0	0.0
10.0	10.0	10.0	0.0	0.0
Total iodine	Fully charged			
[I] (M)	[Na ⁺] ₀ (M)	[I ⁻] ₀ (M)	[I ₃ ⁻] ₀ (M)	[I ₂] ₀ (M)
4.0	1.9048	0.8589	1.0459	1.741×10^{-3}
6.0	2.8571	1.2875	1.5697	1.743×10^{-3}
8.0	3.8095	1.7160	2.0935	1.744×10^{-3}
10.0	4.7619	2.1446	2.6173	1.745×10^{-3}

Table 3: Parameters for modeling the Na-I₂ unit cell

Parameters	Value	Units
Anode		
Thickness (L_a)	1.0	cm
Exchange current factor (i_0°)	12.6	A cm ⁻²
Anodic symmetry factor (α_a)	0.5	
Cathodic symmetry factor (α_c)	0.5	
Cathode		
Thickness (L_c)	1.0	cm
Porosity (ϕ)	0.8	
Fiber diameter (d_f)	10.0	μm
Exchange current factor (i_0°)	1.0	A cm ⁻²
Anodic symmetry factor (α_a)	0.5	
Cathodic symmetry factor (α_c)	0.5	
Rate coefficient $k_{37,\text{f}}$	6.0×10^9	M ⁻¹ s ⁻¹
Separator (NASICON)		
Thickness (L_s)	0.02	cm

Table 4: Summary comparison of charge and discharge processes at different rates

Rate (C)	Charge			Discharge		
	Time (s)	SOC	E_{cell}	Time (s)	SOC	E_{cell}
0.5	6920.5	0.9612	3.2001	7199.0	0.0001	2.4779
1.0	3383.9	0.9400	3.2623	3508.0	0.0256	2.8867
2.5	1085.6	0.7539	3.5891	823.0	0.4285	2.8445
5.0	338.3	0.4698	3.9556	233.0	0.6764	2.6274

Table 5: Summary of charge and discharge behaviors at four total iodine loadings. The current density is fixed $i_{\text{ex}} = 100 \text{ mA cm}^{-2}$

Total iodine	Charge		Discharge	
[I] (M)	Time (s)	SOC	Time (s)	SOC
4.0	1201.2	0.7427	1612.0	0.0033
6.0	2213.2	0.9123	2420.0	0.0024
8.0	3027.7	0.9360	3014.0	0.0682
10.0	3740.0	0.9250	2557.0	0.3676