Solid state battery formulation

1. Formulation

State variables

$$\mathcal{S} = \{\boldsymbol{\varphi}, c_\alpha, \Phi, T\}. \tag{1}$$

Generalized velocities

$$\mathcal{V} = \{\dot{\boldsymbol{\varphi}}, \dot{\boldsymbol{F}}, \dot{c}_\alpha, \boldsymbol{\nabla}\dot{c}_\alpha, \boldsymbol{\nabla}\dot{\Phi}\}. \tag{2}$$

Rate of the total potential is defined as

$$\dot{\Pi} = \int_\Omega \left(\dot{\psi} + \delta^* - T\dot{s} - \chi\right) \, \mathrm{d}V - \mathcal{P}, \tag{3}$$

$$\psi = \psi^m(\boldsymbol{F}, c_\alpha) + \sum_\alpha \psi_\alpha^c(\boldsymbol{F}, c_\alpha, \boldsymbol{\nabla} c_\alpha) + \psi^e(\boldsymbol{F}, \boldsymbol{\nabla}\Phi), \tag{4}$$

$$\delta^* = \psi^{m*}\left(\frac{T}{T^{\mathrm{eq}}}\dot{\boldsymbol{F}}\right) + \sum_\alpha \psi_\alpha^{c\,*}\left(\frac{T}{T^{\mathrm{eq}}}\dot{c}_\alpha, \frac{T}{T^{\mathrm{eq}}}\boldsymbol{\nabla}\dot{c}_\alpha\right) + \psi^{e*}\left(\frac{T}{T^{\mathrm{eq}}}\boldsymbol{\nabla}\dot{\Phi}\right), \tag{5}$$

$$\chi = \frac{\kappa}{2T^2}\boldsymbol{\nabla} T \cdot \boldsymbol{\nabla} T. \tag{6}$$

Thermodynamic forces

$$\mathcal{F} = \{\boldsymbol{P}, \mu_\alpha, \boldsymbol{J}_\alpha, \boldsymbol{D}\}, \tag{7}$$

with (from Coleman-Noll)

$$\boldsymbol{P} = \boldsymbol{P}^{\mathrm{eq}} + \boldsymbol{P}^{\mathrm{vis}}, \quad \mu_\alpha = \mu_\alpha^{\mathrm{eq}} + \mu_\alpha^{\mathrm{vis}}, \quad \boldsymbol{J}_\alpha = \boldsymbol{J}_\alpha^{\mathrm{eq}} + \boldsymbol{J}_\alpha^{\mathrm{vis}}, \quad \boldsymbol{D} = \boldsymbol{D}^{\mathrm{eq}} + \boldsymbol{D}^{\mathrm{vis}}, \tag{8a}$$

$$\boldsymbol{P}^{\mathrm{eq}} = \psi_{,\boldsymbol{F}}, \quad \mu_\alpha^{\mathrm{eq}} = \psi_{,c_\alpha}, \quad \boldsymbol{J}_\alpha^{\mathrm{eq}} = \psi_{,\boldsymbol{\nabla} c_\alpha}, \quad \boldsymbol{D}^{\mathrm{eq}} = \psi_{,\boldsymbol{\nabla}\Phi}, \tag{8b}$$

$$\boldsymbol{P}^{\mathrm{vis}} = \delta^*_{,\dot{\boldsymbol{F}}}, \quad \mu_\alpha^{\mathrm{vis}} = \delta^*_{,\dot{c}_\alpha}, \quad \boldsymbol{J}_\alpha^{\mathrm{vis}} = \delta^*_{,\boldsymbol{\nabla}\dot{c}_\alpha}, \quad \boldsymbol{D}^{\mathrm{vis}} = \delta^*_{,\boldsymbol{\nabla}\dot{\Phi}}. \tag{8c}$$

Balance laws are

$$-\boldsymbol{\nabla}\cdot\boldsymbol{P} - \boldsymbol{b} = \boldsymbol{0}, \tag{9a}$$

$$-\boldsymbol{\nabla}\cdot\boldsymbol{J}_\alpha + \mu_\alpha = 0, \tag{9b}$$

$$-\boldsymbol{\nabla}\cdot\boldsymbol{D} + \rho_q = 0, \tag{9c}$$

$$-\boldsymbol{\nabla}\cdot\boldsymbol{h} + q + \delta + \delta_T = \rho c_v \dot{T}, \tag{9d}$$

where

$$\boldsymbol{h} = -\kappa\boldsymbol{\nabla} T, \tag{10a}$$

$$\delta = \boldsymbol{P}^{\mathrm{vis}} : \dot{\boldsymbol{F}} + \mu_\alpha^{\mathrm{vis}}\dot{c}_\alpha + \boldsymbol{J}_\alpha^{\mathrm{vis}} \cdot \boldsymbol{\nabla}\dot{c}_\alpha + \boldsymbol{D}^{\mathrm{vis}} \cdot \boldsymbol{\nabla}\dot{\Phi}, \tag{10b}$$

$$\delta_T = T\left(\boldsymbol{P}^{\mathrm{eq}}_{,T} : \dot{\boldsymbol{F}} + \mu^{\mathrm{eq}}_{\alpha,T}\dot{c}_\alpha + \boldsymbol{J}^{\mathrm{eq}}_{\alpha,T} \cdot \boldsymbol{\nabla}\dot{c}_\alpha + \boldsymbol{D}^{\mathrm{eq}}_{,T} \cdot \boldsymbol{\nabla}\dot{\Phi}\right) \tag{10c}$$

2. Constitutive models

Yellow ones are kinematical quantities.

Blue ones are energetics.

Red ones are dissipations.

Multiplicative decomposition for swelling and thermal eigenstrains:

$$\boldsymbol{F} = \boldsymbol{F}^e \boldsymbol{F}^s \boldsymbol{F}^t. \tag{11}$$

Note that $\boldsymbol{F}^s$ and $\boldsymbol{F}^t$ are volumetric (diagonal) hence commute. Relevant derivatives:

$$\boldsymbol{F}^e_{,\boldsymbol{F}} = \delta_{ik} {F^g}^{-1}_{lj}, \quad F^g_{ij} = F^s_{ik} F^t_{kj}, \tag{12a}$$

$$\boldsymbol{F}^e_{,\boldsymbol{F}^s} = -{F^e}_{ik} {F^s}^{-1}_{lj}. \tag{12b}$$

Swelling:

$$\boldsymbol{F}^s = (J^s)^{\frac{1}{3}} \boldsymbol{I}, \quad J^s = 1 + \beta^s \sum_\alpha \Omega_\alpha (c_\alpha - c^0_\alpha). \tag{13}$$

Relevant derivatives

$$\boldsymbol{F}^s_{,c_\alpha} = \frac{1}{3} (J^s)^{-\frac{2}{3}} \beta^s \Omega_\alpha \boldsymbol{I}. \tag{14}$$

Neo-Hookean:

$$\psi^m = \frac{1}{2} \lambda \ln^2(I_3) + \frac{1}{2} G \left[I_1 - 2\ln(I_3) - 3 \right], \quad I_1 = \operatorname{tr}\left(F^{eT} F^e \right), \quad I_3 = \det\left(F^e \right). \tag{15}$$

Relevant derivatives:

$$\psi^m_{,\boldsymbol{F}^e} = \lambda \ln(I_3) \boldsymbol{F}^{e-T} + G \left(\boldsymbol{F}^e - \boldsymbol{F}^{e-T} \right), \tag{16a}$$

$$\psi^m_{,\boldsymbol{F}} = \psi^m_{,\boldsymbol{F}^e} : \boldsymbol{F}^e_{,\boldsymbol{F}}, \tag{16b}$$

$$\psi^m_{,c} = \psi^m_{,\boldsymbol{F}^e} : \boldsymbol{F}^e_{,\boldsymbol{F}^s} : \boldsymbol{F}^s_{,c_\alpha}. \tag{16c}$$

Fick's first law of mass transport:

$$\psi^c_\alpha = \frac{1}{2} D_\alpha \boldsymbol{\nabla} c_\alpha \cdot \boldsymbol{\nabla} c_\alpha. \tag{17}$$

Relevant derivatives:

$$\psi^c_{\alpha, \boldsymbol{\nabla} c_\alpha} = D_\alpha \boldsymbol{\nabla} c_\alpha. \tag{18}$$

Mass transport viscosity:

$$\psi^{c\,*}_\alpha = \frac{1}{2} \eta_\alpha \dot{c}^2_\alpha. \tag{19}$$

Relevant derivatives:

$$\psi^{c\,*}_{\alpha,\dot{c}} = \eta_\alpha \dot{c}_\alpha. \tag{20}$$

Polarization:

$$\psi^e = \frac{1}{2} J \varepsilon_0 \varepsilon_r \boldsymbol{e} \cdot \boldsymbol{e}, \quad \boldsymbol{e} = \boldsymbol{F}^{-T} \boldsymbol{\nabla} \Phi. \tag{21}$$

Relevant derivatives:

$$\psi^e_{,\boldsymbol{\nabla}\Phi} = J \varepsilon_0 \varepsilon_r \boldsymbol{C}^{-1} \boldsymbol{\nabla} \Phi, \tag{22a}$$

$$\psi^e_{,\boldsymbol{F}} = J \varepsilon_0 \varepsilon_r \left[\frac{1}{2} (\boldsymbol{e} \cdot \boldsymbol{e}) \boldsymbol{F}^{-T} - \boldsymbol{e} \otimes \boldsymbol{e} \right]. \tag{22b}$$