

# Solid state battery formulation

## 1. Formulation

State variables

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

Generalized velocities

$$\mathcal{V} = \{\dot{\boldsymbol{\varphi}}, \dot{\mathbf{F}}, \dot{c}_\alpha, \nabla \dot{c}_\alpha, \nabla \dot{\Phi}\}. \quad (2)$$

Rate of the total potential is defined as

$$\dot{\Pi} = \int_{\Omega} \left( \dot{\psi} + \Delta^* - T\dot{s} - \chi \right) dV - \mathcal{P}, \quad (3)$$

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

$$\Delta^* = \psi^{m*} \left( \frac{T}{T^{\text{eq}}} \dot{\mathbf{F}} \right) + \sum_{\alpha} \psi_{\alpha}^{c*} \left( \frac{T}{T^{\text{eq}}} \dot{c}_\alpha, \frac{T}{T^{\text{eq}}} \nabla \dot{c}_\alpha \right) + \psi^{e*} \left( \frac{T}{T^{\text{eq}}} \nabla \dot{\Phi} \right), \quad (5)$$

$$\chi = \frac{1}{2} \kappa \frac{\nabla T}{T} \cdot \frac{\nabla T}{T} + \nabla \Phi \cdot \sigma \nabla \Phi \ln(T). \quad (6)$$

Thermodynamic forces

$$\mathcal{F} = \{\mathbf{P}, \mu_\alpha, \mathbf{J}_\alpha, \mathbf{D}\}, \quad (7)$$

with (from Coleman-Noll)

$$\mathbf{P} = \mathbf{P}^{\text{eq}} + \mathbf{P}^{\text{vis}}, \quad \mu_\alpha = \mu_\alpha^{\text{eq}} + \mu_\alpha^{\text{vis}}, \quad \mathbf{J}_\alpha = \mathbf{J}_\alpha^{\text{eq}} + \mathbf{J}_\alpha^{\text{vis}}, \quad \mathbf{D} = \mathbf{D}^{\text{eq}} + \mathbf{D}^{\text{vis}}, \quad (8a)$$

$$\mathbf{P}^{\text{eq}} = \psi_{,\mathbf{F}}, \quad \mu_\alpha^{\text{eq}} = \psi_{,c_\alpha}, \quad \mathbf{J}_\alpha^{\text{eq}} = \psi_{,\nabla c_\alpha}, \quad \mathbf{D}^{\text{eq}} = \psi_{,\nabla \Phi}, \quad (8b)$$

$$\mathbf{P}^{\text{vis}} = \Delta_{,\dot{\mathbf{F}}}^*, \quad \mu_\alpha^{\text{vis}} = \Delta_{,\dot{c}_\alpha}^*, \quad \mathbf{J}_\alpha^{\text{vis}} = \Delta_{,\nabla \dot{c}_\alpha}^*, \quad \mathbf{D}^{\text{vis}} = \Delta_{,\nabla \dot{\Phi}}^*. \quad (8c)$$

Balance laws are

$$-\nabla \cdot \mathbf{P} - \mathbf{b} = \mathbf{0}, \quad (9a)$$

$$-\nabla \cdot \mathbf{J}_\alpha + \mu_\alpha = 0, \quad (9b)$$

$$-\nabla \cdot \mathbf{D} + \rho_q = 0, \quad (9c)$$

$$-\nabla \cdot \mathbf{h} + q + \delta + \delta_T = \rho c_v \dot{T}, \quad (9d)$$

where

$$\mathbf{h} = -\kappa \nabla T, \quad (10a)$$

$$\delta = \mathbf{P}^{\text{vis}} : \dot{\mathbf{F}} + \mu_\alpha^{\text{vis}} \dot{c}_\alpha + \mathbf{J}_\alpha^{\text{vis}} \cdot \nabla \dot{c}_\alpha + \mathbf{D}^{\text{vis}} \cdot \nabla \dot{\Phi}, \quad (10b)$$

$$\delta_T = T \left( \mathbf{P}_{,T}^{\text{eq}} : \dot{\mathbf{F}} + \mu_{\alpha,T}^{\text{eq}} \dot{c}_\alpha + \mathbf{J}_{\alpha,T}^{\text{eq}} \cdot \nabla \dot{c}_\alpha + \mathbf{D}_{,T}^{\text{eq}} \cdot \nabla \dot{\Phi} \right) + \nabla \Phi \cdot \sigma \nabla \Phi. \quad (10c)$$

## 2. Constitutive models

Yellow ones are kinematical quantities.

Blue ones are energetics.

Red ones are dissipations.

Multiplicative decomposition for swelling and thermal eigenstrains:

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^s \mathbf{F}^t. \quad (11)$$

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

$$\mathbf{F}_{,\mathbf{F}}^e = \delta_{ik} F_{lj}^{g-1}, \quad F_{ij}^g = F_{ik}^s F_{kj}^t, \quad (12a)$$

$$\mathbf{F}_{,\mathbf{F}^s}^e = -F_{ik}^e F_{lj}^{s-1}. \quad (12b)$$

Swelling:

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

Relevant derivatives

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

Neo-Hookean:

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

Relevant derivatives:

$$\psi_{,\mathbf{F}^e}^m = \lambda \ln(I_3) \mathbf{F}^{e-T} + G (\mathbf{F}^e - \mathbf{F}^{e-T}), \quad (16a)$$

$$\psi_{,\mathbf{F}}^m = \psi_{,\mathbf{F}^e}^m : \mathbf{F}_{,\mathbf{F}}^e, \quad (16b)$$

$$\psi_{,c}^m = \psi_{,\mathbf{F}^e}^m : \mathbf{F}_{,\mathbf{F}^s}^e : \mathbf{F}_{,c_{\alpha}}^s. \quad (16c)$$

Fick's first law of mass transport:

$$\psi_{\alpha}^c = \frac{1}{2} D_{\alpha} \nabla c_{\alpha} \cdot \nabla c_{\alpha}. \quad (17)$$

Relevant derivatives:

$$\psi_{\alpha, \nabla c_{\alpha}}^c = D_{\alpha} \nabla c_{\alpha}. \quad (18)$$

Mass transport viscosity:

$$\psi_{\alpha}^{c*} = \frac{1}{2} \eta_{\alpha} \dot{c}_{\alpha}^2. \quad (19)$$

Relevant derivatives:

$$\psi_{\alpha, \dot{c}}^{c*} = \eta_{\alpha} \dot{c}_{\alpha}. \quad (20)$$

Polarization:

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

Relevant derivatives:

$$\psi^e_{,\nabla\Phi} = J \varepsilon_0 \varepsilon_r \mathbf{C}^{-1} \nabla \Phi, \quad (22a)$$

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

Redox:

$$\sigma \nabla \Phi \cdot \mathbf{n} = i_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( -\frac{\alpha_c F}{RT} \eta \right) \right], \quad \eta = \Phi_{\text{electrode}} - \Phi_{\text{electrolyte}}. \quad (23)$$