Rate of change of Lithium moles

$$\frac{d}{dt}\int_{\mathcal{R}} c\,\rho\,dV = \frac{d}{dt}\int_{\mathcal{R}_0} c\,\rho\,\underbrace{\det F_0}_{\rho_0}\,dV \qquad\qquad F_0 \equiv \nabla\phi$$

$$= \int_{\mathcal{R}_0}\left(\dot{c}\,\rho + c\,\dot{\rho} + c\,\rho\,\operatorname{div}v\right)\det F_0\,dV$$

$$= \int_{\mathcal{R}_0}\dot{c}\,\rho\,\det F_0\,dV + \int_{\mathcal{R}_0}c\,\underbrace{\left(\dot{\rho} + \rho\,\operatorname{div}v\right)}_{0}\det F_0\,dV$$

$$= \int_{\mathcal{R}_0}\dot{c}\,\rho_0\,dV \qquad = \int_{\mathcal{R}}\dot{c}\,\rho\,dV$$

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Lithium flux

$$\int_{\partial \mathcal{R}} h \cdot n \, dA = \int_{\partial \mathcal{R}_0} (h \cdot n) \left(\frac{A_F}{A_{F_0}}\right) dA = \int_{\partial \mathcal{R}_0} h \cdot (\text{cof} F_0) n_0 \, dA$$

$$= \int_{\partial \mathcal{R}_0} h \cdot F_0^{-T} n_0 \, (\det F_0) \, dA$$

$$= \int_{\partial \mathcal{R}_0} \underbrace{(\det F_0) F_0^{-1} h}_{h_0} \cdot n_0 \, dA$$

$$= \int_{\partial \mathcal{R}_0} h_0 \cdot n_0 \, dA$$

[Notebook page scanned on 2016/06/30]

Species molar balance

$$\frac{d}{dt} \int_{\mathcal{R}} c\rho \, dV = - \int_{\partial \mathcal{R}} h \cdot n \, dA + \int_{\mathcal{R}} h \, dV$$

flux   source

We assume $h = 0$ (no production/reaction)

$$\int_{\mathcal{R}} \dot{c}\rho \, dV = - \int_{\partial \mathcal{R}} h \cdot n \, dA$$

$$\int_{\mathcal{R}_0} \dot{c}\rho_0 \, dV = - \int_{\partial \mathcal{R}_0} h_0 \cdot n_0 \, dA$$

which localize to

$$\dot{c}\rho + \operatorname{div} h = 0 \qquad\qquad \text{in } \mathcal{R}$$

$$\dot{c}\rho_0 + \operatorname{div} h_0 = 0 \qquad\qquad \text{in } \mathcal{R}_0$$

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From molar balance to power balance

Let us introduce a scalar field (chemical potential)

$$\mu_o(x) = \mu(\phi(x))$$

"energy per mole of Lithium"

in order to turn the species molar balance into
a power molar balance:

$$\int_{\mathcal{R}} (\dot{c}\rho + \mathrm{div}\, h)\, \mu \; dV = 0 \qquad \forall \mu$$

$$\int_{\mathcal{R}_o} (\dot{c}\rho_o + \mathrm{div}\, h_o)\, \mu_o \; dV = 0 \qquad \forall \mu_o$$

$$\Rightarrow \qquad \int_{\mathcal{R}_o} \mu_o\, \dot{c}\rho_o \, dV = -\int_{\mathcal{R}_o} \mathrm{div}\,(\mu_o h_o)\, dV + \int_{\mathcal{R}_o} h_o \cdot \nabla \mu_o \, dV = 0$$

$$\int_{\mathcal{R}_o} \mu_o\, \dot{c}\rho_o \, dV = -\int_{\partial \mathcal{R}_o} \mu_o\, h_o \cdot n_o \, dA + \int_{\mathcal{R}_o} h_o \cdot \nabla \mu_o \, dV = 0$$

with $\quad \mathrm{div}\,(\mu_o h_o) = \mathrm{tr}\left(\nabla(\mu_o h_o)\right) = \mathrm{tr}\left(\mu_o \nabla h_o + \nabla \mu_o \otimes h_o\right)$

$$= \mu_o\, \mathrm{div}\, h_o + h_o \cdot \nabla \mu_o$$

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Power balance laws

$$\int_{\mathcal{R}_0} b_0 \cdot v_0 \, dV + \int_{\partial \mathcal{R}_0} t_0 \cdot v_0 \, dA = \int_{\mathcal{R}_0} S_0 \cdot \nabla v_0 \, dV \qquad \forall v_0$$

$$\underbrace{\hspace{6cm}}_{\text{external power expenditure}} \qquad [\to G.(27.20)]$$

$$\int_{\mathcal{R}_0} \mu_0 \dot{c} \, \rho_0 \, dV = -\int_{\partial \mathcal{R}_0} \mu_0 h_0 \cdot n_0 \, dA + \int_{\mathcal{R}_0} h_0 \cdot \nabla \mu_0 \, dV \qquad \forall \mu_0$$

$$\underbrace{\hspace{6cm}}_{\text{external power expenditure}}$$

Free energy imbalance principle:

for any constitutive process (for any realizable evolution)

$$S_0 \cdot \dot{F}_0 + \mu_0 \dot{c} \rho_0 - h_0 \cdot \nabla \mu_0 - \frac{d}{dt} \psi \geqslant 0$$

[very general expression]

Let us assume

$$\psi = \hat{\psi}(F_0, c)$$

and

$$\frac{d}{dt} \hat{\psi}(F_0, c) = S_0 \cdot \dot{F}_0 + \mu_0 \rho_0 \dot{c}$$

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Fick's law

Because of the previous assumption the free energy imbalance reduces to

$$-h_o \cdot \nabla\mu_o \geq 0$$

which must be fulfilled in any realizable evolution.

This requirement leads to the following characterization of the molar flux
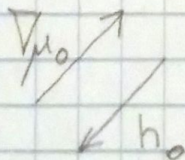
$$h_o = -M\nabla\mu_o \qquad \text{Fick's law}$$

with M a positive definite tensor (mobility)
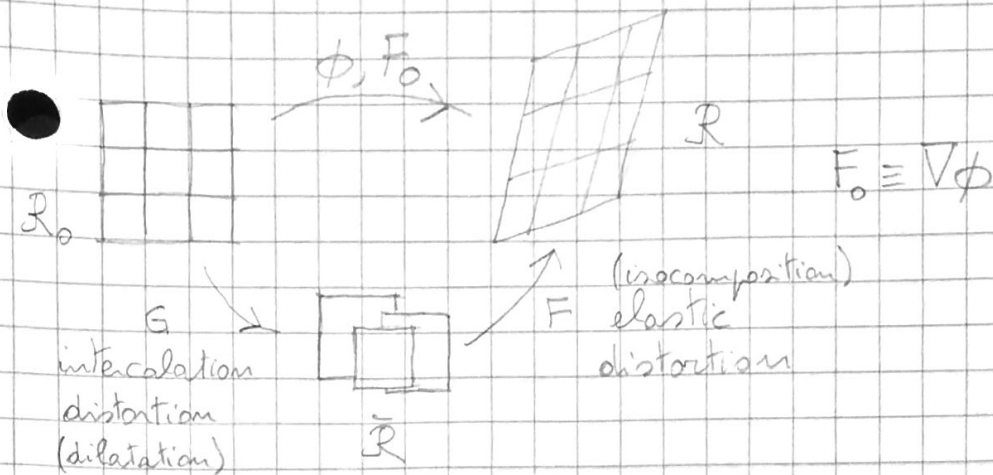
$$M\nabla\mu_o \cdot \nabla\mu_o \geq 0$$

As a special case we get

$$h_o = -d\,\nabla\mu_o$$

with $d \geq 0$ (diffusion coefficient)

$$\phi, F_0 \longrightarrow$$

$$\mathcal{R}$$

$$\mathcal{R}_0$$

$$F_0 = \nabla \phi$$

G (intercalation distortion (dilatation))

F (isocompositional) elastic distortion

$$\tilde{\mathcal{R}}$$

$$\beta = \det G \qquad G = \beta^{1/3} I$$

$$F_0 = FG$$

stoichiometric constant $\longleftarrow$

$$\det G = \left(\rho_0 V_0 + \rho_{li} V_{li} \right) / \left(\rho_0 V_0 \right) = 1 + c\, \frac{V_{li}}{V_0} = 1 + c\, \alpha$$

$$\dot\beta = \alpha \dot c \qquad \frac{d}{dt}\left(\det G \right) = \left(\det G \right) \mathrm{tr}\left(\dot G G^{-1} \right) = \ldots = \alpha \dot c$$

$$\dot G G^{-1} = \frac{1}{3} \beta^{-\frac{2}{3}} \beta^{-\frac{1}{3}} \alpha \dot c\, I = \frac{1}{3} \frac{\alpha}{\beta} \dot c\, I$$

$$\dot F_0 F_0^{-1} = \left(\dot F G + F \dot G \right) G^{-1} F^{-1} = \dot F F^{-1} + \frac{1}{3} \frac{\alpha}{\beta} \dot c\, I$$

$$S_0 = T F_0^{-T} \left(\det F_0 \right) \qquad\qquad S = T F^{-T} \left(\det F \right)$$

$$S_0 \cdot \dot F_0 = \left(\det F_0 \right) T F_0^{-T} \cdot \dot F_0 = \beta \left(\det F \right) T \cdot \dot F_0 F_0^{-1}$$

$$= \beta \left(\det F \right) T \cdot \dot F F^{-1} + \frac{1}{3} \alpha \left(\det F \right) T \cdot I\, \dot c$$

$$= \beta\, S \cdot \dot F + \frac{1}{3} \alpha \left(\det F \right) \mathrm{tr}\, T\, \dot c$$

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Hence, according to the previous assumptions
about the free energy, we get

$$\frac{d}{dt} \hat{\psi}(F_0, c) = S_0 \cdot \dot{F}_0 + \mu_0 \rho_0 \dot{c}$$

$$= \beta S \cdot \dot{F} + \left(\frac{1}{3} \alpha (\det F) \, tr \, T + \mu_0 \rho_0 \right) \dot{c}$$

If we further assume for the free energy
the expression

$$\hat{\psi}(F_0, c) = (\det G) \, \varphi(F)$$

with

$$\frac{d}{dt} \varphi(F) = S \cdot \dot{F}$$

we finally get

$$\beta \frac{d}{dt} \varphi(F) + \dot{\beta} \, \varphi(F)$$

$$= \beta S \cdot \dot{F} + \left(\frac{1}{3} \alpha (\det F) \, tr \, T + \mu_0 \rho_0 \right) \dot{c}$$

$$\left(\frac{1}{3} \alpha (\det F) \, tr \, T - \alpha \, \varphi(F) + \mu_0 \rho_0 \right) \dot{c} = 0$$

$$\Rightarrow \quad \mu_0 = \frac{\alpha}{\rho_0} \left(\varphi(F) - \frac{1}{3} (\det F)(tr \, T) \right)$$

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We could start directly from the free energy expression

$$\psi = (\det G)\,\varphi(F) \qquad \det G = \beta$$

$$\frac{d}{dt}\psi = \dot{\beta}\,\varphi(F) + \beta\frac{d}{dt}\varphi(F) = \dot{\beta}\,\varphi(F) + \beta\,\hat{S}(F)\cdot\dot{F}$$

$$\dot{F}_0 = \frac{d}{dt}\left(F\beta^{1/3}\right) = \beta^{1/3}\dot{F} + \frac{1}{3}\beta^{-2/3}\dot{\beta}\,F$$

$$\beta^{2/3}\dot{F}_0 = \beta\dot{F} + \frac{1}{3}\dot{\beta}\,F$$

$$\beta\,\hat{S}(F)\cdot\dot{F} = \hat{S}(F)\cdot\left(\beta^{2/3}\dot{F}_0 - \frac{1}{3}\dot{\beta}\,F\right)$$

$$S_0 = (\det G)\,S\,G^{-T} = \beta S \beta^{-1/3} = \beta^{2/3}S$$

$$\beta\,\hat{S}(F)\cdot\dot{F} = \hat{S}_0(F)\cdot\dot{F}_0 - \frac{1}{3}\hat{S}(F)F^T\cdot I\,\dot{\beta}$$

$$S = (\det F)\,T\,F^{-T} \;\Rightarrow\; \hat{S}(F)F^T\cdot I = (\det F)\,\text{tr}\,\hat{T}(F)$$

$$\beta\,\hat{S}(F)\cdot\dot{F} = \hat{S}_0(F)\cdot\dot{F}_0 - \frac{1}{3}(\det F)\,\text{tr}\,\hat{T}(F)\,\dot{\beta}$$

We get also

$$\beta S\cdot\dot{F} = S_0\cdot\dot{F}_0 - \frac{1}{3}(\det F)(\text{tr}\,T)\,\dot{\beta}$$

$$[\,2015\text{-}11\text{-}16\,]$$

From the free energy imbalance

$$S_o \cdot \dot{F}_o + \mu_o \rho_o \dot{c} - h_o \cdot \nabla \mu_o - \frac{d}{dt} \psi \geq 0$$

we get

$$\beta \, S \cdot \dot{F} + \frac{1}{3} (\det F)(tr\,T) \dot{\beta} + \mu_o \rho_o \dot{c} - h_o \cdot \nabla \mu_o$$

$$- \varphi \dot{\beta} - \beta \, \hat{S}(F) \cdot \dot{F} \geq 0$$

Rearranging terms

$$\beta \left(S - \hat{S}(F) \right) \cdot \dot{F} + \left(\frac{1}{3}(\det F)(tr\,T) - \varphi \right) \dot{\beta} + \mu_o \rho_o \dot{c}$$

$$- h_o \cdot \nabla \mu_o \geq 0$$

Let us set now $\beta = 1 + \alpha c$

This relationship between concentration and volume change is a stoichiometric relation about the intercalation of atoms in a lattice cell, when describing the diffusion of a species in a lattice.

In poroelasticity the relation above is nothing but the saturation condition.

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Further, relying on the assumption

$$\beta = 1 + \alpha c$$

we can introduce a new balance law

$$\int_{\mathcal{R}_0} \left(\check{P}_0 \dot{\beta} - \mu_0 \rho_0 \dot{c} \right) dV = 0 \quad \forall \dot{c}$$

relating the power expended by an interstitial pressure to the rate of change of the energy transported by a diffusing species.

The local form of the balance law is

$$\alpha \check{P}_0 = \mu_0 \rho_0 \qquad \Rightarrow \qquad \mu_0 = \frac{\alpha}{\rho_0} \check{P}_0$$

Denoting by J and p $\quad J = \det F, \ p = -\frac{1}{3} \left(\operatorname{tr} T \right),$

the free energy imbalance takes the form

$$\beta \underbrace{\left(S - \hat{S}(F) \right) \cdot \dot{F}}_{S^+} + \underbrace{\left(-Jp - \psi + \check{P}_0 \right) \dot{\beta}}_{\check{P}_0^+} - \frac{\alpha}{\rho_0} h_0 \cdot \nabla \check{P}_0 \geqslant 0$$

or, equivalently,

$$\beta S^+ \cdot \dot{F} + \check{P}_0^+ \dot{\beta} - \frac{\alpha}{\rho_0} h_0 \cdot \nabla \check{P}_0 \geqslant 0$$

[2016-11-18]

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with

$$S = \hat{S}(F) + S^{\dagger}$$

$$\check{p}_0 = \varphi + Jp + \check{p}_0^{\dagger}$$

characterizing the stress and the interstitial pressure through $S^{\dagger}$ and $\check{p}_0^{\dagger}$, dissipative terms subject in any process to the dissipation inequality above.
As a consequence we obtain as separate conditions

$$S^{\dagger} \cdot \dot{F} \geq 0$$

$$\check{p}^{\dagger} \dot{\beta} \geq 0 \qquad (\dot{\beta} \text{ is independent of } \dot{F})$$

$$-\frac{\alpha}{\rho_0} h_0 \cdot \nabla \check{p}_0 \geq 0 \qquad (\text{to cover the case where } \dot{\beta}=0, \dot{F}=0)$$

Since

$$S^{\dagger} \cdot \dot{F} = S^{\dagger} F^{T} \cdot \dot{F} F^{-1} = J^{-1} T^{\dagger} \cdot \dot{F} F^{-1}$$

a standard choice is

$$T^{\dagger} = 2\mu_s \operatorname{sym}(\dot{F} F^{-1}) \qquad \text{with } \mu_s \geq 0$$

leading to

$$T^{\dagger} \cdot \dot{F} F^{-1} \geq 0$$

Similarly we can choose

$$\check{p}_0^{\dagger} = \mu_v \dot{\beta} \qquad \text{with } \mu_v \geq 0$$

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In order to fulfil the last inequality we arrive at the Darcy's law

$$h_o = -M \nabla \mu_o = -M \frac{\alpha}{\rho_o} \nabla \check{p}_o$$

as a variant of the Fick's law resulting from the special choice of the free energy expression.

Denoting by V^m the molar volume of the interstitial species in the reference shape we may define the discharge per unit reference area

$$q_o = h_o V^m$$

and get

$$q_o = -V^m \frac{\alpha}{\rho_o} M \nabla \check{p}_o$$

The corresponding units of measure turn out to be

$$[q_o] = \left(m^3 mol^{-1}\right)\left(mol^{-1} m^3\right)\left(s^{-1} mol^2 P_a^{-1} m^{-4}\right)\left(P_a m^{-1}\right)$$

$$= m^6 mol^{-2} s^{-1} mol^2 m^{-5} = s^{-1} m$$

The total discharge is $Q_o = q_o A \Rightarrow [Q_o] = m^3 s^{-1}$

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Unit of measure

$$[h] = mol\ m^{-2}\ s^{-1}$$

$$[\mu] = J\ mol^{-1}$$

$$[\mu\ \dot{c}\ \rho] = J\ mol^{-1}\ s^{-1}\ mol\ m^{-3} = J\ mol^{-3}\ s^{-1}$$

$$[h\ \nabla\mu] = (mol\ m^{-2}\ s^{-1})(J\ mol^{-1}\ m^{-1}) = J\ m^{-3}\ s^{-1}$$

$$h = -M\ \nabla\mu$$

$$\Rightarrow\ [M] = (mol\ m^{-2}\ s^{-1})(J\ mol^{-1}\ m^{-1})^{-1} = J^{-1}\ mol^{2}\ m^{-1}\ s^{-1}$$

molar volume

$$[V^{mm}] = m^{3}\ mol^{-1}$$

discharge

$$[q] = (m^{3}\ mol^{-1})(mol\ m^{-2}\ s^{-1}) = m\ s^{-1}$$

amount of matter measured by   mol

As an alternative it can be measured by Kg

[2016-12-17]

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