1 Mass Conservation in the Solid

We assume that mass within V can be changed only by allowing it to enter or exit through the boundary S.

$$\oiint_S \mathbf{N} \cdot \hat{\mathbf{n}}\, \mathrm{d}S = -j = -\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}t} \iiint_V c\, \mathrm{d}V = -\iiint_V \left(\frac{\partial c}{\partial t}\right) \mathrm{d}V.$$

We divide both sides of the equation by V and take the limit as the volume shrinks to zero:

$$\nabla \cdot \mathbf{N} = \lim_{V \to 0} \frac{1}{V} \oiint_S \mathbf{N} \cdot \hat{\mathbf{n}}\, \mathrm{d}S = -\lim_{V \to 0} \frac{1}{V} \iiint_V \left(\frac{\partial c}{\partial t}\right) \mathrm{d}V = -\frac{\partial c}{\partial t}$$

We assume that for the movement of lithium atoms within either the negative- or positive-electrode active material crystalline structures, it occurs due to interstitial diffusion only. That is, we assume that molar flux density $\mathbf{N}$ is proportional to the concentration gradient ∇c via Fick's first law:

$$\mathbf{N} = -D\nabla c,$$

which gives the mass conservation equation (known as Fick's second law)

$$\frac{\partial c}{\partial t} = \nabla \cdot D\nabla c.$$

2 Charge Conservation in the Solid

We assume that charge within V can be changed only by allowing it to enter or exit through the boundary S.

$$\oiint_S \mathbf{i} \cdot \hat{\mathbf{n}}\, \mathrm{d}S = -i = -\frac{\mathrm{d}Q}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}t} \iiint_V \rho_V\, \mathrm{d}V = -\iiint_V \left(\frac{\partial \rho_V}{\partial t}\right) \mathrm{d}V.$$

We divide both sides of the equation by V and take the limit as the volume shrinks to zero:

$$\nabla \cdot \mathbf{i} = \lim_{V \to 0} \frac{1}{V} \oiint_S \mathbf{i} \cdot \hat{\mathbf{n}}\, \mathrm{d}S = -\lim_{V \to 0} \frac{1}{V} \iiint_V \left(\frac{\partial \rho_V}{\partial t}\right) \mathrm{d}V = -\frac{\partial \rho_V}{\partial t} = 0.$$

Here, we assume the rate of electron movement in the solid lattice is much faster than the rate of other processes in the electrochemical cell. Therefore, ρ_V reaches an equilibrium state relatively quickly and $\partial\rho/\partial t \approx 0$. Next, based on Ohm's law, current density $\mathbf{i}$ is proportional to the applied electric field $\mathbf{E}$:

$$\mathbf{i} = \sigma\mathbf{E} = -\sigma\nabla\phi,$$

which gives the charge conservation equation in the solid

$$\nabla \cdot \sigma\nabla\phi = 0.$$

3 Mass Conservation in the Electrolyte

The electrolyte is formulated by dissolving a charge-neutral solute into a charge-neutral solvent. Here, the electrolyte is considered to be binary electrolyte, that is, one having exactly two charged constitutes. The binary electrolyte comprises the solvent (0), the positively charged ions (cations) and the negatively charged ions (anions). For either cations (+) or anions (−), the mass continuity equation holds,

$$\frac{\partial c_+}{\partial t} = -\nabla \cdot \mathbf{N}_+ \Rightarrow \frac{\partial c}{\partial t} = -\frac{1}{\nu_+}\nabla \cdot \mathbf{N}_+. \tag{1}$$

The flux density of cations can be expressed as

$$\mathbf{N}_+ = -\nu_+ \frac{\mathcal{D} c_T}{c_0}\left(1 + \frac{\mathrm{d}\ln\gamma_\pm}{\mathrm{d}\ln m}\right)\left(1 - \frac{\mathrm{d}\ln c_0}{\mathrm{d}\ln c}\right)\nabla c + \frac{\mathbf{i} t_+^0}{z_+ F} + c_+\mathbf{v}_0. \tag{2}$$

As a result, the mass conservation equation is

$$\begin{aligned}\frac{\partial c}{\partial t} &= \nabla \cdot \left(\frac{\mathcal{D} c_T}{c_0}\left(1 + \frac{\mathrm{d}\ln\gamma_\pm}{\mathrm{d}\ln m}\right)\left(1 - \frac{\mathrm{d}\ln c_0}{\mathrm{d}\ln c}\right)\nabla c\right) - \nabla \cdot \frac{\mathbf{i} t_+^0}{z_+\nu_+ F} - \nabla \cdot \left(\frac{c_+}{\nu_+}\mathbf{v}_0\right) \\ &= \underbrace{\nabla \cdot \left(\frac{\mathcal{D} c_T}{c_0}\left(1 + \frac{\mathrm{d}\ln\gamma_\pm}{\mathrm{d}\ln m}\right)\left(1 - \frac{\mathrm{d}\ln c_0}{\mathrm{d}\ln c}\right)\nabla c\right)}_{\text{diffusion}} - \underbrace{\frac{\mathbf{i}\cdot\nabla t_+^0}{z_+\nu_+ F}}_{\text{migration}} - \underbrace{\nabla \cdot (c\mathbf{v}_0)}_{\text{convection}}\end{aligned} \tag{3}$$

We can see that the concentration changes due to three causes:

- diffusion: ions move because of a concentration gradient
- migration: ions move due to effects of an electric field
- convection: ions move subject to a pressure gradient—solute ions are pulled along by the movement of the solvent

In contrast, the concentration change in the solid is only subject to diffusion.

$$\mathbf{N}_+ = c_+\mathbf{v}_+ = -\frac{\nu_+\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i} t_+^0}{z_+ F} + c_+\mathbf{v}_0 \tag{4}$$

with

$$\nabla\mu_e = \frac{\nu RT}{c}\left(1 + \frac{d\ln\gamma_\pm}{d\ln m}\right)\left(1 - \frac{d\ln c_0}{d\ln c}\right)\nabla c \tag{5}$$

$$\mathbf{N}_+ = c_+\mathbf{v}_+ = \frac{\mathbf{i}_+}{z_+F} = \frac{\mathbf{i} - \mathbf{i}_-}{z_+F} = \frac{\mathbf{i} - z_-Fc_-\mathbf{v}_-}{z_+F} = \frac{\mathbf{i}}{z_+F} + \frac{z_+c_+F\mathbf{v}_-}{z_+F} = \frac{\mathbf{i}}{z_+F} + c_+\mathbf{v}_- \tag{6}$$

$$= \frac{K_{0+}}{K_{0+}+K_{0-}}c_+\mathbf{v}_+ + \frac{K_{0-}}{K_{0+}+K_{0-}}\left(\frac{\mathbf{i}}{z_+F} + c_+\mathbf{v}_-\right) + c_+\mathbf{v}_0 - c_+\mathbf{v}_0 \tag{7}$$

$$= \underbrace{\frac{K_{0+}}{K_{0+}+K_{0-}}c_+\mathbf{v}_+ + \frac{K_{0-}}{K_{0+}+K_{0-}}c_+\mathbf{v}_- - c_+\mathbf{v}_0}_{-\frac{\nu_+\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e} + \underbrace{\frac{K_{0-}}{K_{0+}+K_{0-}}}_{t_+^0}\frac{\mathbf{i}}{z_+F} + c_+\mathbf{v}_0 \tag{8}$$

$$\frac{K_{0+}}{K_{0+}+K_{0-}}c_+\mathbf{v}_+ + \frac{K_{0-}}{K_{0+}+K_{0-}}c_+\mathbf{v}_- - c_+\mathbf{v}_0 \tag{9}$$

$$= c_+\frac{K_{0+}\mathbf{v}_+ + K_{0-}\mathbf{v}_- - K_{0+}\mathbf{v}_0 - K_{0-}\mathbf{v}_0}{K_{0+}+K_{0-}} \tag{10}$$

$$= -c_+\frac{K_{0+}(\mathbf{v}_0-\mathbf{v}_+) + K_{0-}(\mathbf{v}_0-\mathbf{v}_-)}{K_{0+}+K_{0-}} \tag{11}$$

$$= -c_+\frac{K_{+0}(\mathbf{v}_0-\mathbf{v}_+) + K_{+-}(\mathbf{v}_- - \mathbf{v}_+) + K_{-0}(\mathbf{v}_0-\mathbf{v}_-) + K_{-+}(\mathbf{v}_+ - \mathbf{v}_-)}{K_{0+}+K_{0-}} \tag{12}$$

$$= -c_+\frac{c_+\nabla\bar{\mu}_+ + c_-\nabla\bar{\mu}_-}{K_{0+}+K_{0-}} = -c_+\frac{c(\nu_+\nabla\bar{\mu}_+ + \nu_-\nabla\bar{\mu}_-)}{K_{0+}+K_{0-}} \tag{13}$$

$$= -c_+\frac{c\left(\nu_+\nabla(\mu_+ + z_+F\phi) + \nu_-\nabla(\mu_- + z_-F\phi)\right)}{K_{0+}+K_{0-}} \tag{14}$$

$$= -c_+\frac{c\left(\nu_+\nabla\mu_+ + \nu_-\nabla\mu_-\right)}{K_{0+}+K_{0-}} = -\frac{c_+}{K_{0+}+K_{0-}}c\nabla\mu_e \tag{15}$$

$$= -\frac{\nu_+\frac{\nu RTc_0c}{c_T(K_{+0}+K_{-0})}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e = -\frac{\nu_+\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e \tag{16}$$

$$\nabla\mu_e = \frac{\partial\mu_e}{\partial c}\nabla c = \frac{\partial\mu_e}{\partial\ln m}\frac{\partial\ln m}{\partial c}\nabla c \tag{17}$$

$$\frac{\partial\mu_e}{\partial\ln m} = \frac{\partial\left(\nu_+\mu_+ + \nu_-\mu_-\right)}{\partial\ln m} \tag{18}$$

$$= \frac{\partial\left(\nu_+RT\ln(m_+\gamma_+\lambda_+^{\ominus}) + \nu_-RT\ln(m_-\gamma_-\lambda_-^{\ominus})\right)}{\partial\ln m} \tag{19}$$

$$= \frac{\partial\left(\nu_+RT\ln(m\nu_+\gamma_+\lambda_+^{\ominus}) + \nu_-RT\ln(m\nu_-\gamma_-\lambda_-^{\ominus})\right)}{\partial\ln m} \tag{20}$$

$$= \frac{\partial\left(\nu_+RT\ln(m\gamma_+) + \nu_-RT\ln(m\gamma_-)\right)}{\partial\ln m} \tag{21}$$

$$= \frac{\partial\left(\nu_+RT(\ln m + \ln\gamma_+) + \nu_-RT(\ln m + \ln\gamma_-)\right)}{\partial\ln m} \tag{22}$$

$$= \frac{\partial\left((\nu_+ + \nu_-)RT\ln m + RT(\ln\gamma_+^{\nu_+} + \ln\gamma_-^{\nu_-})\right)}{\partial\ln m} \tag{23}$$

$$= \frac{\partial\left(\nu RT\ln m + RT\ln\gamma_\pm^{\nu}\right)}{\partial\ln m} = \nu RT\left(1 + \frac{\partial\ln\gamma_\pm}{\partial\ln m}\right) \tag{24}$$

$$\frac{\partial\ln m}{\partial c} = \frac{\partial\ln\frac{m_+}{\nu_+}}{\partial c}\nabla c = \frac{\partial\ln\frac{c_+}{\nu_+c_0M_0}}{\partial c}\nabla c = \frac{\partial\ln\frac{c}{c_0M_0}}{\partial c}\nabla c \tag{25}$$

$$= \frac{\partial(\ln c - \ln c_0 - \ln M_0)}{\partial\ln c}\frac{\partial\ln c}{\partial c}\nabla c = \frac{1}{c}\left(1 - \frac{d\ln c_0}{d\ln c}\right)\nabla c \tag{26}$$

$$\nabla\mu_e = \frac{\nu RT}{c}\left(1 + \frac{\partial\ln\gamma_\pm}{\partial\ln m}\right)\left(1 - \frac{d\ln c_0}{d\ln c}\right)\nabla c \tag{27}$$

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \frac{\mathbf{i} \cdot \nabla t_+^0}{F} - \nabla \cdot (c \mathbf{v}_0)$$

with

$$D = \frac{\mathcal{D} c_T}{c_0} \left(1 + \frac{d \ln \gamma_\pm}{d \ln m}\right) \left(1 - \frac{d \ln c_0}{d \ln c}\right) \tag{28}$$

4 Charge Conservation in the Electrolyte

$$\frac{\partial c_+}{\partial t} = -\nabla \cdot \mathbf{N}_+. \tag{29}$$

$$\nabla \cdot \mathbf{i} = \nabla \cdot (z_+ F \mathbf{N}_+ + z_- F \mathbf{N}_-) = z_+ F \nabla \cdot \mathbf{N}_+ + z_- F \nabla \cdot \mathbf{N}_- \tag{30}$$

$$= -z_+ F \frac{\partial c_+}{\partial t} - z_- F \frac{\partial c_-}{\partial t} = -F \frac{\partial (z_+ c_+ + z_- c_-)}{\partial t} = 0 \tag{31}$$

$$\mathbf{i} = -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_+}{n \nu_+} - \frac{s_0 c}{n c_0} + \frac{t_+^0}{\nu_+ z_+} \right) \nabla \mu_e \tag{32}$$

with

$$\nabla \mu_e = \underbrace{\nu R T \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c}\right)}_{\frac{\partial \mu_e}{\partial \ln c}} \nabla \ln c \tag{33}$$

$$\begin{aligned}
\frac{\partial u_e}{\partial \ln c} &= \frac{\partial \left(\nu_+ \bar{\mu}_+ + \nu_- \bar{\mu}_-\right)}{\partial \ln c} = \frac{\partial \left(\nu_+ (\mu_+ + z_+ F \phi) + \nu_- (\mu_- + z_- F \phi)\right)}{\partial \ln c} \\
&= \frac{\partial \left(\nu_+ (RT \ln(c_+ f_+ a_+^\ominus) + z_+ F \phi) + \nu_- (RT \ln(c_- f_- a_-^\ominus) + z_- F \phi)\right)}{\partial \ln c} \\
&= \frac{\partial \left(\nu_+ (RT \ln(c \nu_+ f_+ a_+^\ominus) + z_+ F \phi) + \nu_- (RT \ln(c \nu_- f_- a_-^\ominus) + z_- F \phi)\right)}{\partial \ln c} \\
&= \frac{\partial \left(\nu_+ (RT \ln(c f_+) + z_+ F \phi) + \nu_- (RT \ln(c f_-) + z_- F \phi)\right)}{\partial \ln c} \\
&= \frac{\partial \left(\nu_+ (RT (\ln c + \ln f_+) + z_+ F \phi) + \nu_- (RT (\ln c + \ln f_-) + z_- F \phi)\right)}{\partial \ln c} \\
&= \nu_+ \left(RT + RT \frac{\partial \ln f_+}{\partial \ln c} + z_+ F \frac{\partial \ln \phi}{\partial \ln c}\right) + \nu_- \left(RT + RT \frac{\partial \ln f_-}{\partial \ln c} + z_- F \frac{\partial \ln \phi}{\partial \ln c}\right) \\
&= (\nu_+ + \nu_-) RT + RT \left(\frac{\partial \ln f_+^{\nu_+}}{\partial \ln c} + \frac{\partial \ln f_-^{\nu_-}}{\partial \ln c}\right) + (\nu_+ z_+ + \nu_- z_-) F \frac{\partial \ln \phi}{\partial \ln c} \\
&= \nu RT + RT \frac{\partial \ln f_\pm^\nu}{\partial \ln c} = \nu RT \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c}\right)
\end{aligned}$$

$$
\begin{aligned}
&s_+\nabla\bar{\mu}_+ + s_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = s_+\nabla\bar{\mu}_+ + \frac{-n - s_+z_+}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{z_+\nu_+}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{-z_-\nu_-}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+ + \nu_-\nabla\bar{\mu}_-\right) - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}c_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_0 - \mathbf{v}_-) + K_{+-}(\mathbf{v}_+ - \mathbf{v}_-)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_- - \mathbf{v}_0) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0))\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(\frac{K_{0-}}{c_-}\left(-\frac{\nu_-\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0))\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(\frac{K_{0-}}{c_-}\left(-\frac{\nu_-\frac{\nu RTc_0c}{c_T(K_{0+}+K_{0-})}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0))\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\Bigg(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) \\
&\quad - K_{+-}\left(\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_+^0}{c_+z_+F}\right) - \left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right)\right)\Bigg) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} - \frac{t_-^0}{c_-z_-}\right)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} + \frac{1-t_+^0}{c_+z_+}\right)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{c_+z_+F}\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{nc}{z_-c_-}\frac{K_{0-}}{K_{0+}+K_{0-}}\nabla\mu_e - \frac{K_{0-}t_-^0 + K_{+-}}{c_-z_-c_+z_+F}n\mathbf{i} + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nct_+^0}{c_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - s_0\frac{c_+\nabla\bar{\mu}_+ + c_-\nabla\bar{\mu}_-}{c_0} \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nt_+^0}{\nu_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - \frac{s_0c}{c_0}\nabla\mu_e = -nF\nabla\phi
\end{aligned}
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\begin{aligned}
&s_+\nabla\bar{\mu}_+ + s_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = s_+\nabla\bar{\mu}_+ + \frac{-n - s_+z_+}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{z_+\nu_+}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{-z_-\nu_-}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+ + \nu_-\nabla\bar{\mu}_-\right) - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}c_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_0 - \mathbf{v}_-) + K_{+-}(\mathbf{v}_+ - \mathbf{v}_-)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_- - \mathbf{v}_0) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0))\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(\frac{K_{0-}}{c_-}\left(-\frac{\nu_-\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(\frac{K_{0-}}{c_-}\left(-\frac{\nu_-\frac{\nu RTc_0c}{c_T(K_{0+}+K_{0-})}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\Bigg(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) \\
&\quad - K_{+-}\left(\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_+^0}{c_+z_+F}\right) - \left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right)\right)\Bigg) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} - \frac{t_-^0}{c_-z_-}\right)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} + \frac{1-t_+^0}{c_+z_+}\right)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{c_+z_+F}\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{nc}{z_-c_-}\frac{K_{0-}}{K_{0+}+K_{0-}}\nabla\mu_e - \frac{K_{0-}t_-^0 + K_{+-}}{c_-z_-c_+z_+F}n\mathbf{i} + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nct_+^0}{c_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - s_0\frac{c_+\nabla\bar{\mu}_+ + c_-\nabla\bar{\mu}_-}{c_0} \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nt_+^0}{\nu_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - \frac{s_0c}{c_0}\nabla\mu_e = -nF\nabla\phi
\end{aligned}
$$

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\begin{aligned}
&s_+\nabla\bar{\mu}_+ + s_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = s_+\nabla\bar{\mu}_+ + \frac{-n - s_+z_+}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{z_+\nu_+}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+\right) - \frac{n}{z_-}\nabla\bar{\mu}_- - \frac{s_+}{\nu_+}\left(\frac{-z_-\nu_-}{z_-}\nabla\bar{u}_-\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\left(\nu_+\nabla\bar{\mu}_+ + \nu_-\nabla\bar{\mu}_-\right) - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-}\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 = \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}c_-\nabla\bar{\mu}_- + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_0 - \mathbf{v}_-) + K_{+-}(\mathbf{v}_+ - \mathbf{v}_-)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}(\mathbf{v}_- - \mathbf{v}_0) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0)\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{n}{z_-c_-}\left(K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{c_+z_+F}\right) + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e - \frac{nc}{z_-c_-}\frac{K_{0-}}{K_{0+}+K_{0-}}\nabla\mu_e - \frac{K_{0-}t_-^0 + K_{+-}}{c_-z_-c_+z_+F}n\mathbf{i} + s_0\nabla\bar{\mu}_0 \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nct_+^0}{c_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - s_0\frac{c_+\nabla\bar{\mu}_+ + c_-\nabla\bar{\mu}_-}{c_0} \\
&= \frac{s_+}{\nu_+}\nabla\mu_e + \frac{nt_+^0}{\nu_+z_+}\nabla\mu_e + \frac{nF}{\kappa}\mathbf{i} - \frac{s_0c}{c_0}\nabla\mu_e = -nF\nabla\phi
\end{aligned}
$$

$$
K_{0-}(\mathbf{v}_- - \mathbf{v}_0) - K_{+-}\left((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0)\right) \tag{34}
$$

$$
= \frac{K_{0-}}{c_-}\left(-\frac{\nu_-\mathcal{D}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0) \tag{35}
$$

$$
\begin{aligned}
&= \frac{K_{0-}}{c_-}\left(-\frac{\nu_-\frac{\nu RTc_0c}{c_T(K_{0+}+K_{0-})}}{\nu RT}\frac{c_T}{c_0}c\nabla\mu_e + \frac{\mathbf{i}t_-^0}{z_-F}\right) - K_{+-}((\mathbf{v}_+ - \mathbf{v}_0) - (\mathbf{v}_- - \mathbf{v}_0) \\
&= K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) \\
&\quad - K_{+-}\left(\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_+^0}{c_+z_+F}\right) - \left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right)\right) \\
&= K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} - \frac{t_-^0}{c_-z_-}\right) \\
&= K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{F}\left(\frac{t_+^0}{c_+z_+} + \frac{1-t_+^0}{c_+z_+}\right) \\
&= K_{0-}\left(-\frac{c}{K_{0+}+K_{0-}}\nabla\mu_e + \frac{\mathbf{i}t_-^0}{c_-z_-F}\right) - K_{+-}\frac{\mathbf{i}}{c_+z_+F}
\end{aligned}
$$

$$\mathbf{i} = -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_+}{n\nu_+} + \frac{t_+^0}{\nu_+ z_+} - \frac{s_0 c}{n c_0} \right) \tag{36}$$

with

$$\kappa = -\frac{c_- z_- c_+ z_+ F^2}{K_{0-} t_-^0 + K_{+-}} \tag{37}$$

$$\nabla \cdot (-\kappa \nabla \phi_e - \kappa_D \nabla \ln c_e) = 0 \tag{38}$$

with

$$\kappa_D = \frac{2\kappa RT(t_+^0 - 1)}{F} \tag{39}$$