Let's consider the deposition of Cu^{2+} from the solution of $CuCl_2$ and HCl. Let's define:

$[CuCl_2] = c_{13}^b$ and $[HCl] = c_{23}^b$.

Hence: $[Cu^{2+}] = c_1$, $[H^+] = c_2$ and $[Cl^-] = c_3$. When $c_{13}^b \ll c_{23}^b$, Cu^{2+} is a trace ion and the limiting current density is given as [1]

$$I_{L0} = -\frac{2FD_1 c_1^b}{\delta} \tag{1}$$

where δ is the thickness of the diffusion boundary layer. When only species 1 is reactive at the electrode the Nernst-Planck equations are (1D case) [1]:

$$j_1 = \frac{I}{z_1 F} = -D_1\left(\frac{dc_1}{dx} + z_1 f c_1 \frac{d\phi}{dx}\right) \tag{2}$$

$$j_k = 0 = -D_k\left(\frac{dc_k}{dx} + z_k f c_k \frac{d\phi}{dx}\right) \quad ; \quad k \neq 1 \tag{3}$$

where $f = F/RT$. From eq. (3), the concentration profile can be integrated as

$$c_k(x) = c_k^b e^{z_k f[\phi^b - \phi(x)]} \quad \Rightarrow \quad c_k(x) = c_k^b e^{z_k f \Delta\phi} \quad ; \quad k \neq 1 \tag{4}$$

where $\Delta\phi$ is the potential drop in the diffusion boundary layer. It can be show [1] that the current density is given as:

$$\frac{I}{z_1 F} = \frac{D_1}{\delta}\sum_{k\neq 1}\left(1 - \frac{z_k}{z_1}\right) c_k^b \left(e^{z_k f \Delta\phi} - 1\right) \tag{5}$$

Applying the above equation to our case, it is obtained that

$$\frac{I}{2F} = \frac{D_1}{\delta}\left[\frac{1}{2} c_2^b \left(e^{f\Delta\phi} - 1\right) + \frac{3}{2} c_3^b \left(e^{-f\Delta\phi} - 1\right)\right] \tag{6}$$

At the limiting current $c_1(0) = 0$, which means via electroneutrality that $c_2(0) = c_3(0)$. Using eq. (4):

$$c_2^b e^{f\phi_L} = c_3^b e^{-f\phi_L} \quad \Leftrightarrow \quad e^{f\phi_L} = \sqrt{\frac{c_3^b}{c_2^b}} \tag{7}$$

Inserting this to eq. (6), the limiting current density is given as

$$\begin{aligned} \frac{I_L}{2F} &= \frac{D_1}{2\delta}\left[c_2^b\left(\sqrt{\frac{c_3^b}{c_2^b}} - 1\right) + 3c_3^b\left(\sqrt{\frac{c_2^b}{c_3^b}} - 1\right)\right] = \frac{D_1}{2\delta}\left[\left(\sqrt{c_2^b c_3^b} - c_2^b\right) + 3\left(\sqrt{c_2^b c_3^b} - c_3^b\right)\right] \\ &= \frac{D_1}{2\delta}\left[4\sqrt{c_2^b c_3^b} - c_2^b - 3c_3^b\right] = \frac{D_1}{2\delta}\left[4\sqrt{c_{23}^b\left(2c_{13}^b + c_{23}^b\right)} - 4c_{23}^b - 6c_{13}^b\right] \end{aligned} \tag{6}$$

because $c_2^b = c_{23}^b$ and $c_3^b = 2c_{13}^b + c_{23}^b$. Modifying further:

$$I_L = \frac{4FD_1c_{13}^b}{\delta}\left[\sqrt{\frac{1}{r}\left(2+\frac{1}{r}\right)}-\frac{1}{r}-\frac{3}{2}\right] \quad ; \quad r = \frac{c_{13}^b}{c_{23}^b} \tag{7}$$

In the limiting case $r \to \infty$ the system is binary (only $CuCl_2$) the limiting current density is

$$I_L = -\frac{6FD_1c_{13}^b}{\delta} = 3I_{L0} \tag{8}$$

For the trace case, eq. (6) is better to write as follows:

$$I_L = \frac{4FD_1c_{23}^b}{\delta}\left[\sqrt{2r+1}-1-\frac{3}{2}r\right] \tag{9}$$

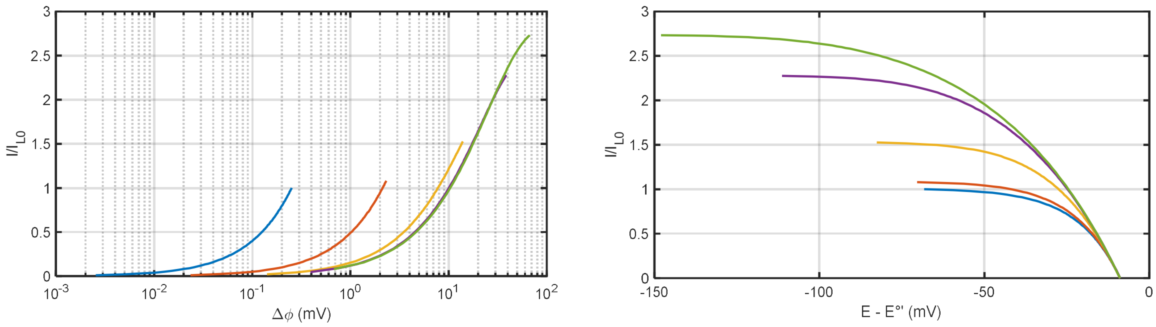
When $r \to 0$, $\sqrt{2r+1} \to 1+r$ which then recovers eq. (1) as expected. For computer simulations, the following form is useful

$$\frac{I}{I_{L0}} = -\left[\frac{1}{2r}\left(e^{f\Delta\phi}-1\right)+3\left(1+\frac{1}{2r}\right)\left(e^{-f\Delta\phi}-1\right)\right] \tag{10}$$

The surface concentration of H^+ and Cl^- can be calculated from eq. (4) and that of Cu^{2+} from the electroneutrality condition $2c_1 + c_2 = c_3$. The electrode potential can then be calculated from the Nernst equation as

$$E = E^{0'} + \frac{RT}{2F}\ln\left(\frac{c_1(0)}{c^*}\right) \tag{11}$$

where c^* is the standard concentration 1.0 M. The total potential is $E - \Delta\phi$ because we defined $\Delta\phi$ as $\phi^b - \phi(0)$ but the electrode potential is defined $\phi_{electrode} - \phi_{solution}$. Hence, giving values for $\phi < \phi_L$ the full current-voltage can be simulated.



Left: Potential drop in the diffusion double layer; r = 100 (green), 10 (cyan), 1 (yellow), 0.1 (orange), 0.01 (blue). Right: Current-voltage curves; color code the same.

[1] K. Kontturi, L. Murtomäki, J.A. Manzanares, Ionic Transport Processes, Oxford University Press, 2008, pp. 85-87.