Supplementary Information

Supplementary Information: High-frequency current distribution on the boundary between two different conductivity materials

A cylindrical (radius = R, height = Z) coordinate system is used to analyse the high-frequency current density characteristics at the boundary of different conductive materials. Equation 1 is derived from Ohm's law: if the current density $\boldsymbol{i} = (i_z, i_r, i_\theta)$, electric field strength $\boldsymbol{E} = (E_z, E_r, E_\theta)$ and electrical conductivity $\sigma(z)$ are functions that fluctuate only in the Z direction,

$$\boldsymbol{i} = \boldsymbol{\sigma}(\boldsymbol{z})\boldsymbol{E}, \tag{1}$$

$$\boldsymbol{\nabla} \times \boldsymbol{i} = \boldsymbol{\nabla} \times \sigma(z)\boldsymbol{E}. \tag{2}$$

Equation 2 can be described as Eqs. 3, 4 and 5 using Maxwell's equations $\boldsymbol{\nabla} \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial \boldsymbol{t}} = -\mu \frac{\partial \boldsymbol{H}}{\partial \boldsymbol{t}}$, and Ampere's law $\boldsymbol{\nabla} \times \boldsymbol{H} = \boldsymbol{i}$, where $\boldsymbol{B} = (B_z, B_r, B_\theta)$ is the magnetic flux density, μ is the material permeability, $\boldsymbol{H} = \mu^{-1}\boldsymbol{B}$ is the magnetic field strength.

$$\boldsymbol{\nabla} \times \boldsymbol{i} = -\sigma(z)\mu \frac{\partial \boldsymbol{H}}{\partial t}, \tag{3}$$

$$\boldsymbol{\nabla} \times \boldsymbol{\nabla} \times \boldsymbol{i} = -\sigma(z)\mu \frac{\partial \boldsymbol{\nabla} \times \boldsymbol{H}}{\partial t}, \tag{4}$$

$$\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{i}) - \boldsymbol{\nabla}^2 \boldsymbol{i} = -\sigma(z)\mu \frac{\partial \boldsymbol{i}}{\partial t}. \tag{5}$$

Current continuity ($\boldsymbol{\nabla} \cdot \boldsymbol{i} = \boldsymbol{0}$) simplifies Eq. 5 to Eqs. 6 and 7:

$$\boldsymbol{\nabla}^2 \boldsymbol{i} = \sigma(z)\mu \frac{\partial \boldsymbol{i}}{\partial t}, \tag{6}$$

$$\frac{\partial^2 \boldsymbol{i}}{\partial r^2} + \frac{1}{r}\frac{\partial \boldsymbol{i}}{\partial r} + \frac{1}{r^2}\frac{\partial \boldsymbol{i}}{\partial \theta} + \frac{\partial^2 \boldsymbol{i}}{\partial z^2} = \sigma(z)\mu \frac{\partial \boldsymbol{i}}{\partial t}. \tag{7}$$

Finally, the behaviour of AC is described using Eq. 8 and $\boldsymbol{i} = \boldsymbol{I}e^{j\omega t}$:

$$\frac{\partial^2 \boldsymbol{I}}{\partial r^2} + \frac{1}{r}\frac{\partial \boldsymbol{I}}{\partial r} + \frac{1}{r^2}\frac{\partial \boldsymbol{I}}{\partial \theta} + \frac{\partial^2 \boldsymbol{I}}{\partial z^2} = j\sigma(z)\mu\omega\boldsymbol{I}. \quad (8)$$

Using Eq. 8, we estimate the current distribution on the σ interface. In the wide cylinder model, aspect $R >> Z$ allows $\frac{1}{r}\frac{\partial \boldsymbol{I}}{\partial r} \approx 0$, and symmetry allows $i_\theta = 0$.

If $\sigma(z)$ is a constant independent of z, then Eq. 8 can be represented as follows:

$$\frac{\partial^2 \boldsymbol{I}}{\partial r^2} = j\sigma(z)\mu\omega\boldsymbol{I}, \quad (9)$$

where

$$\boldsymbol{I} = Ae^{\left(\sqrt{\frac{\sigma(z)\mu\omega}{2}} \pm j\sqrt{\frac{\sigma(z)\mu\omega}{2}}\right)r}. \quad (10)$$

The well-known skin effect (Eq. 11) can be derived from Eq. 10.

$$\boldsymbol{I} = Ae^{\left(\sqrt{\frac{\sigma(z)\mu\omega}{2}}\right)r.} \quad (11)$$

In the battery model, $\sigma(z)$ in the layered materials is not constant and induces additional current distribution along the r axis. Based on the above equations, we observed a trend in $\boldsymbol{i_r}$ at each $\sigma(z)$ boundary. In each region, $\boldsymbol{i_z}$ attempts to distribute according to Eq. 12. In the boundary zone, $\boldsymbol{i_r}$ flows and varies continuously at the same time. The current continuity ($\boldsymbol{\nabla \cdot i = 0}$) changes the relation between $\boldsymbol{i_r}$ and $\boldsymbol{i_z}$:

$$\boldsymbol{\nabla} \cdot \boldsymbol{i} = \frac{\partial \boldsymbol{i_z}}{\partial z} + \frac{1}{r}\frac{\partial r\boldsymbol{i_r}}{\partial r} + \frac{1}{r}\frac{\partial r\boldsymbol{i_\theta}}{\partial \theta} = 0$$

$$\frac{\partial \boldsymbol{i_z}}{\partial z} = -\frac{1}{r}\frac{\partial r\boldsymbol{i_r}}{\partial r}, \quad (12)$$

where i_θ is set to 0. When each region has $\sigma(z_1) = \sigma_1$ and $\sigma(z_2) = \sigma_2$, the approximated current $I_z = I_z(z, r)$ and $I_r = I_r(z, r)$ can be calculated in the neighborhood of the boundary $\Delta z = z_1 - z_2$,

$$\frac{\partial \boldsymbol{I_z}}{\partial z} = \frac{I_z(z_1, r) - I_z(z_2, r)}{z_1 - z_2}$$

$$= \frac{A(z_1)e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r} - A(z_2)e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r}}{\Delta z}$$

$$= -\frac{1}{r}\frac{\partial r I_r\left(\frac{z_1 + z_2}{2}, r\right)}{\partial r}, \qquad (13)$$

where $A(z)$ denotes area-specific constant amplitudes. The total current in the z direction $\int_0^{2\pi}\int_0^R I_z(z,r) r dr d\theta = constant$; hence, satisfy Eq. 15,

$$\int_0^{2\pi}\int_0^R A(z_1)e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r} r dr d\theta = \int_0^{2\pi}\int_0^R A(z_2)e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r} r dr d\theta \quad (14)$$

$$A(z_1)\left\{\frac{2}{\sigma_1 \mu \omega} e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)R}\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}} R - 1\right) + \frac{2}{\sigma_1 \mu \omega}\right\}$$

$$= A(z_2)\left\{\frac{2}{\sigma_2 \mu \omega} e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)R}\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}} R - 1\right) + \frac{2}{\sigma_2 \mu \omega}\right\}. (15)$$

The trend of the boundary current $\boldsymbol{i_r}$ can be derived by reformulating Eqs. 13 and 15,

$$\frac{\partial r I_r\left(\frac{z_1 + z_2}{2}, r\right)}{\partial r} = \frac{-A(z_1)e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r} + A(z_2)e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r}}{\Delta z} r \qquad (16)$$

$$r I_r\left(\frac{z_1 + z_2}{2}, r\right) = \int \frac{-A(z_1)e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r} + A(z_2)e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r}}{\Delta z} r dr$$

$$= \frac{-\frac{A(z_1)2}{\sigma_1 \mu \omega} e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r}\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}} r - 1\right) + \frac{A(z_2)2}{\sigma_2 \mu \omega} e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r}\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}} r - 1\right)}{\Delta z}$$

$$I_r\left(\frac{z_1 + z_2}{2}, r\right) = \frac{-\frac{A(z_1)2}{\sigma_1 \mu \omega} e^{\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}}\right)r}\left(\sqrt{\frac{\sigma_1 \mu \omega}{2}} r - 1\right) + \frac{A(z_2)2}{\sigma_2 \mu \omega} e^{\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}}\right)r}\left(\sqrt{\frac{\sigma_2 \mu \omega}{2}} r - 1\right)}{r \Delta z}. (17)$$

When σ_1 is the conductivity of the active material and σ_2 is the conductivity of the electrolytic solution, we can estimate the vertical current of the electrolytic solution layer as $I_z(z_2, r) = constant \; = \; B$ with $\sigma_2\mu\omega \ll \sigma_1\mu\omega$. Then, Eq. 17 is simplified as follows:

$$I_r\left(\frac{z_1+z_2}{2}, r\right) = \frac{-\frac{A(z_1)2}{\sigma_1\mu\omega} e^{\left(\sqrt{\frac{\sigma_1\mu\omega}{2}}\right)r}\left(\sqrt{\frac{\sigma_1\mu\omega}{2}}r - 1\right) + \frac{1}{2}Br^2}{r\Delta z}, \tag{18}$$

where $A(z_1)$ can be described by B in Eq. 15:

$$A(z_1) = \frac{BR^2\frac{\sigma_1\mu\omega}{2}}{2\left(e^{\left(\sqrt{\frac{\sigma_1\mu\omega}{2}}\right)R}\left(\sqrt{\frac{\sigma_1\mu\omega}{2}}R - 1\right) + 1\right)}. \tag{19}$$

Equation 18 summarizes the trend of the current distribution in the surface direction (r) on the higher conductivity surface of different conductivity materials. Moreover, this current is increased monotonically by σ_1. Consequently, the Li-metal plating that increases the digits of σ_1 significantly changes the H_z of a battery.

Supplementary Table 1: Specifications of the tested batteries

Model name	NCR18650b	INR18650 M26	IFR18650EC-1.5Ah
Sample name	NCA	NCM	LFP
Battery type	18650		
Anode material	Graphite		
Cathode material	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	$LiNi_{0.49}Co_{0.2}Mn_{0.31}O_2$	$LiFePO_4$
Nominal voltage	3.6 V	3.65 V	3.2 V
Cutoff voltage	2.5–4.2 V	2.75–4.2 V	2–3.65 V
Nominal capacity	3350 mAh	2600 mAh	1500 mAh
Weight	48.5 g	44.0 g	42.0 g
Standard charge current	1625 mA	1.250 mA	300 mA
Max charge current	1675 mA	2500 mA	3000 mA

Supplementary Table 2: Degradation conditions of the 18650 batteries

Sample name	**NCA**		**NCM**		**LFP**	
Degradation name	Rapid charge cycle	High-temperature cycle	Rapid charge cycle	Rapid charge cycle with sensor	Rapid charge cycle	High-temperature cycle
Temperature	20 ˚C	60 ˚C	20˚C	20˚C	20˚C	60˚C
CC charge	6700 mA (2 C) Cutoff 4.2 V	1675 mA (0.5 C) Cutoff 4.2 V	5200 mA (2 C) Cutoff 4.2 V	5200 mA (2 C) Cutoff 4.3 V	6000 mA (4 C) Cutoff 3.9 V	750 mA (0.5 C) Cutoff 3.65 V
CC discharge	335 mA (0.1 C) Cutoff 2.5 V	1675 mA (0.5 C) Cutoff 2.5 V	260 mA (0.1 C) Cutoff 2.75 V	1300 mA (0.5 C) Cutoff 2.85 V	150 mA (0.1 C) Cutoff 2.0 V	750 mA (0.5 C) Cutoff 2.0 V
CV discharge	2.5 V 3 h	-	2.75 V 3 h	2.85 V 3 h	2.0 V 3 h	-
Rest time after charge/discharge	10 min	10 min	10 min	10 min	10 min	10 min
Cycle number	12–63	80–575	5–90	31	6–30	20–300