



Heterogeneity in MacMullin Number of Li-Ion Battery Electrodes Studied by Means of an Aperture Probe

Baichuan Liu,¹ Kayci Prugue,¹ Mojdeh Nikpour,¹ Kristopher Ward,² Brian A. Mazzeo,² and Dean R. Wheeler^{1,*}

¹Chemical Engineering Department, Brigham Young University, Provo, Utah

²Electrical and Computer Engineering Department, Brigham Young University, Provo, Utah

Heterogeneity of MacMullin number within battery electrodes is a key metric affecting cell performance. To characterize this heterogeneity, an aperture probe was developed. This probe, coupled with a newly developed transmission-line model, allows for measurements of tortuosity, represented by the MacMullin number, on millimeter length scales. Local MacMullin number values of seven electrodes were measured, and the ionic resistance profiles of these electrodes are given through contour maps of the MacMullin number. The method is validated by comparing the average MacMullin number to the value obtained through other measurement methods. The results show significant local MacMullin number variation in such electrodes on a millimeter length scale. This method will allow battery manufacturers and researchers to better quantify sources of heterogeneity and improve electrode quality.

© 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ac4542]

Manuscript submitted October 16, 2021; revised manuscript received December 11, 2021. Published January 14, 2022. This was Paper 255 presented at the Atlanta, Georgia, Meeting of the Society, October 13–17, 2019.

Tortuosity is a dimensionless number used to characterize the ionic transport pathways in porous electrodes.¹ High tortuosity lowers the effective ionic conductivity of electrolytes and the effective diffusivity of lithium ions inside porous electrodes.^{2,3} Low lithium-ion diffusivity causes depletion of lithium ions near the electrode-electrolyte interface for cathodes during fast discharge and for anodes during fast charge, which limits the practical capacity of the battery. In addition, the depletion of lithium ions near the surface of an anode is one factor that favors lithium plating.⁴ Therefore, to improve the performance of a battery, tortuosity is a key aspect that needs to be studied and understood.

Heterogeneity of tortuosity is of particular interest in this research. A growing amount of effort has been devoted to studying the heterogeneity of electrode structures^{5–8} and of charge-transfer reactions.^{9–12} Forouzan et al.¹³ studied the effects of the structural heterogeneity of electrodes using a Newman-type model and applied it simultaneously to multiple regions of the electrode. Their research suggests that heterogeneity contributes to non-uniform lithium plating that causes dendrite growth. Such plating on the negative electrode is a significant cause of battery degradation.¹⁴ The study conducted by Gogoana et al.¹⁵ suggests that a 20% difference between the internal resistance of two matched cells could reduce the life span of the cell by 40%. Therefore, understanding and addressing the problem of heterogeneity can help improve battery performance.

To measure the heterogeneity of battery electrode properties, researchers have been exploring the application of scanning electrochemical microscopy (SECM) to the visualization of Li-ion concentration,^{16,17} electrochemical properties,^{18–22} and SEI formation^{23,24} at the nanoscale. Hossain et al.²⁵ applied SECM, together with a redox agent, to measure the effective diffusivity of ions in porous electrodes at a micrometer scale. By computing the ratio of effective diffusion coefficient to the bulk diffusion coefficient of redox agent, they computed MacMullin numbers of porous electrodes, and their results were in agreement with the theoretical values (Bruggeman model) when the porosity is above 60%.

There are two primary methods used to quantify tortuosity. One approach involves numerically estimating the tortuosity based on tomographic data.^{26–30} Another approach is to directly measure transport phenomena of the composite material, such as the ionic conductivity and the diffusivity.^{2,31–33,34–38} Pouraghajan et al.³ refined the blocking-electrolyte method originally developed by Landesfeind et

al.¹² to quantify the tortuosity of battery electrodes. However, the blocking-electrolyte method does not measure the heterogeneity of tortuosity, since the model for the blocking-electrolyte method assumes a homogeneous microstructure. Thus, we developed a new instrument, called "aperture probe", to directly measure the tortuosity at different locations of an electrode. The principle of the aperture probe is to generate a large amount of current from a high-surface-area electrode inside the aperture probe, converge all the current to the aperture, and drive the current to the electrode sample within a small area limited by the dimension of the aperture. (see Fig. 1). The mechanism of the new instrument is similar to that of the blocking-electrolyte method, but the measurable area is smaller, yielding a higher spatial resolution (approximately 400 μm).

Tortuosity is represented in this research as a MacMullin number, which is the ratio of the tortuosity to the porosity (see Eq. 1). The MacMullin number is used because it does not require any assumption about porosity and is directly used in any Newman-type transport model.^{35,39,40,31} The MacMullin number is defined as

$$N_m = \frac{k_{\text{int}}}{k} = \frac{\tau}{\epsilon} \quad [1]$$

where k_{int} is the intrinsic ionic conductivity of the electrolyte, k is the effective ionic conductivity in the porous electrode, τ is the tortuosity, and ϵ is the porosity.

In this work, we present the structure and the fabrication of the aperture probe and the local tortuosity measurement process. A new model to analyze the local impedance data is explained. The local tortuosity measurement technique is validated by comparing the average tortuosity value obtained from the localized measurement technique to the value obtained from the blocking-electrolyte method and other references. Finally, we generate contour maps that reveal the tortuosity variation of seven representative battery electrodes and perform statistical analysis on the heterogeneity of the electrodes measured.

Aperture Probe and Experiment

Aperture Probe Design.—Additional design elements of the aperture probe are illustrated in Fig. 2. The "T" shaped main body of the aperture probe is machined from Teflon (the blue object in part (a) and part (b)). The internal structure of the aperture probe is shown in Fig. 2b. The core component of the aperture probe is a stack of silver membranes (Sterlitech, 5.0 micrometer pore size) that has a porous structure and high internal surface area to generate a large amount of current. There are 10 layers of silver membrane

*Electrochemical Society Member.

^zE-mail: dean_wheeler@byu.edu

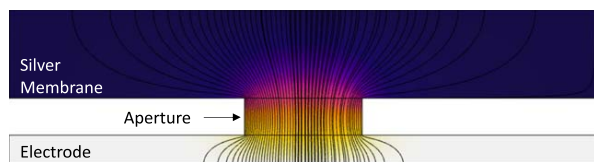


Figure 1. Operating principle of aperture probe. The color scale from dark purple to white represents the electrochemical potential in three regions: silver membrane, aperture, and electrode. The black solid lines show the current density and current direction across the three regions.

placed in the compartment of the aperture probe, each a disc of 3.18 mm diameter. The stacked silver membranes are connected to a current source through an external copper wire (orange line in Figs. 2a, 2b). A polyimide film (125 μm thick) is covering the silver membranes and is sealed to the probe by epoxy (J-B WaterWeld). In the center of the polyimide film, there is an aperture cut with a drill bit (400 μm diameter). The effective diameter of the aperture in this research is 404 μm , which is calculated from the area of the aperture observed in the optical image shown in Fig. 2c.

Experiment setup.—Figure 3 illustrates the configuration of the measurement stage and the experiment setup. Accurate position control of the probe is important. As shown in Fig. 3a, an XYZ-controlled stage (Newmark Systems Inc. ET-150-14 for X and Y controllers, Actuatorix Pg-12 with feedback for Z controller) was constructed and the aperture probe was mounted to the XYZ-controlled stage. Positioning is accurate within 0.6 μm over 1 mm of travel and has a resolution of 0.24 μm . The XYZ-controlled stage was computer-controlled through a custom Python program.

In the Petri dish filled with electrolyte, an electrode sample is located below the movable stage on a larger sheet of copper foil used to connect the electrode to the current source. A 10-layer silver membrane stack is placed next to the electrode sample (see Fig. 3b) for a probe calibration measurement explained in the next section. The electrolyte used in this research is 25.8 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) in propylene carbonate (Sigma Aldrich). The Petri dish, together with the actuator stage, is covered with a plastic film to reduce evaporation of the solvent. An

Table I. Definitions of Variables from Eq. 1 to 34.

Variable	Definition
N_m	MacMullin Number
r	r axis of cylindrical coordinate system
z	z axis of cylindrical coordinate system
τ	Tortuosity of battery electrode
ϵ	Porosity of battery electrode
σ	Effective electronic conductivity of porous electrode
k_{int}	Intrinsic ionic conductivity of electrolyte
k	Effective ionic conductivity of electrolyte in electrode
ϕ_1	Electric potential of solid phase
ϕ_2	Electric potential of liquid phase
i_1	Current density of solid phase
i_2	Current density of liquid phase
z_s	Charge transfer impedance
R_{ct}	Faradaic resistance
Q_s	Constant phase element parameter
A_s	Constant phase element order
f	Alternating current frequency
j	Imaginary part of complex number
r_o	Outer radius of model geometry
r_i	Inner radius of model geometry (radius of the aperture)
t	Thickness of the porous sample
t_f	Thickness of the polyimide film
α	Anisotropy factor
G	Constant current density at aperture
ΔV	Potential difference between aperture and current collector
V_{aperture}	Average potential at aperture
I	Amount of current from external power supply
p	Value of parameter
Z_{Exp}	Experimental impedance value

isothermal heat sink was placed beneath the Petri dish to fix the temperature at 20 $^{\circ}\text{C}$ during the measurement.

Experiment samples.—To validate the localized ionic conductivity measurement and the inversion technique and explore electrode

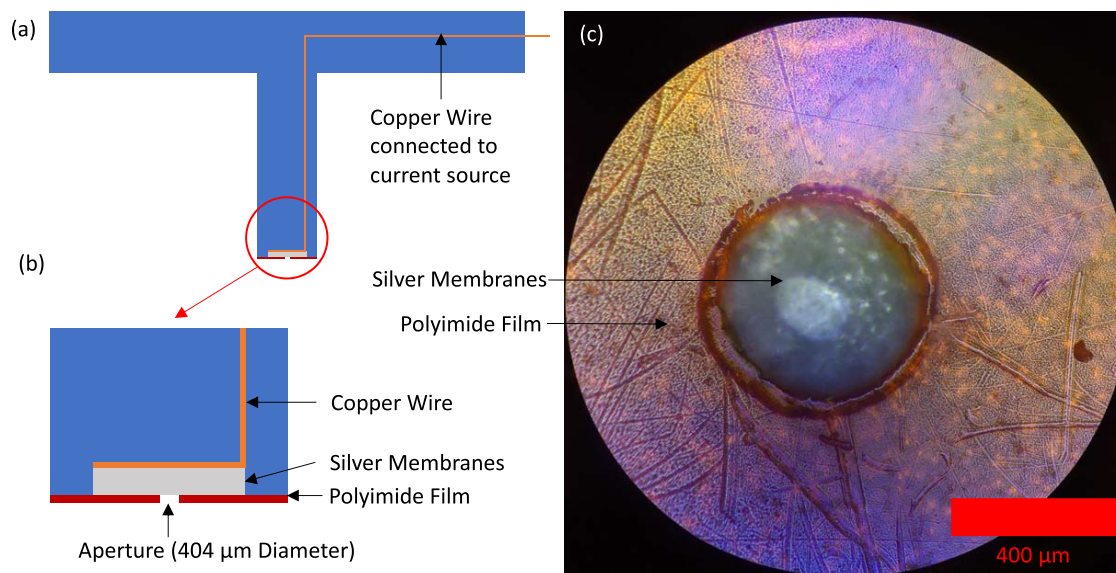


Figure 2. (a) The side cross-section of the structure of the aperture probe. (b) Zoomed view of the compartment of the aperture probe (inside the red circle of part (a)). (c) Image of the aperture under an optical microscope. A silver membrane is visible inside the aperture but is blurred due to the lens focus of the microscope.

Exhibit 2005

Ningde Ampere Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 2 of 13

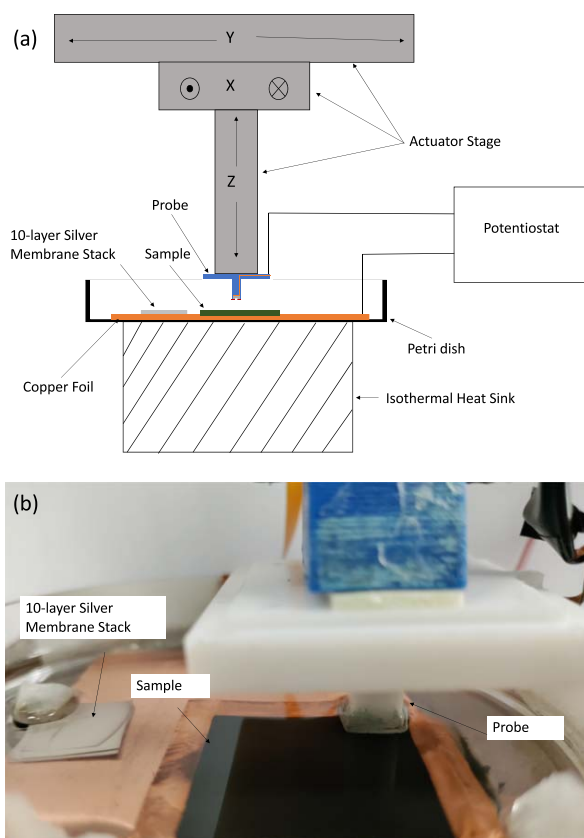


Figure 3. (a) Schematic of measurement stage and experiment setup. The probe is mounted in an inverted configuration and descends onto the sample. The plastic film that covers the setup is not shown. (b) Layout of the sample, 10-layer silver membrane stack, and the probe inside the Petri dish.

heterogeneity, we scanned 7 electrodes. Table II gives descriptions for each electrode. The AC006, AA005, Round-2 anode (R2-A), and Round-2 cathode (R2-C) were provided by Argonne National Laboratory. R2-A and R2-C were specially made for fast-charging research. HQ LCO was prepared and supplied by Hydro-Quebec. We measured the thickness of the electrode films with a micrometer (the listed thickness excludes the thickness of the current collector). The porosity of the electrodes was provided by the manufacturers. However, to test the aperture probe with a larger tortuosity range, we increased the tortuosity of R2-A and R2-C by further calendering these two electrodes (R2+A and R2+C). The porosity of these adjusted electrodes was extrapolated from the porosity reported by the manufacturer according to the change in thickness.

Bulk-average MacMullin number measurement using the blocking-electrolyte method.—First, the blocking-electrolyte method

was used to benchmark the MacMullin number of each electrode. As described in the previous work of Pouraghajan et al.,³ a 4 cm² piece of electrode and a second, slightly larger electrode, were cut. A separator was placed between these electrodes, and the stack was placed into a pouch. Each piece had an uncoated current collector tab protruding outside the sealed pouch to be used for electrical connection. The same electrolyte used for localized measurements was injected into the pouch cell. Finally, the pouch was sealed using an electric heat sealer.

After sitting for 24 h to allow wetting, each pouch cell was measured under an external pressure of 33.4 kPa, which is calculated based on the weight (1.36 kg) placed on the sample and the size of the sample (4 cm²), using an EIS instrument (Bio-Logic SP 200) with a perturbation of 50 mV and frequencies varying with logarithmic spacing from 3 MHz to 0.1 Hz. The open-circuit potential for the symmetric cell was measured as zero, and so no DC bias was used. The bulk average MacMullin number of each electrode was obtained through impedance data inversion with a 1D transmission-line model. For HQ LCO, we used the reported tortuosity value³ as a benchmark. For R2-A and R2-C, the bulk-average MacMullin numbers were obtained from the electrodes that are not the same piece, but respectively the same batch, of the electrodes used for localized measurement, because the R2 electrodes used in this study needed to remain intact for other research.

Localized tortuosity measurement.—After finishing the pouch cell measurements, we opened the pouch cells and used the aperture probe to measure the local tortuosity of each piece of electrode from the pouch cell. The localized ionic measurement was conducted by moving the aperture probe to each assigned location and lowering the probe down to the surface of the electrode until the aperture made contact with the electrode. A typical contact pressure between probe and sample is 73 kPa, which is the ratio of contact force (26.3 N) and the contact area (36 mm²). While in contact, an EIS spectrum was collected with frequencies varying from 4 kHz to 0.3 Hz and perturbation of 50 mV. The open-circuit potential between the aperture probe and the sample was in the order of 10 mV, and so no DC bias was applied. After the measurement, impedance data were fit to MacMullin numbers using the 2D transmission-line model.

The local EIS equivalent circuits are the same for both blocking-electrolyte method and localized tortuosity measurement, but one is solved in cylindrical geometry versus 1D Cartesian geometry. The diagram of the circuit is displayed in Fig. 5 from the publication by Pouraghajan et al.³

Contour plots of MacMullin number of each electrode were generated using a self-developed MATLAB program, assuming a linear variation of MacMullin number between adjacent test locations.

Probe calibration.—To measure and calibrate the aperture probe impedance, the probe was programmed to regularly measure the 10-layer silver membrane stack placed next to the sample (see Fig. 3b) during the electrode scan, using the same EIS measurement settings used for the electrode measurement.

Table II. Composition, film thickness, and porosity values for cathodes and anodes tested in this work. The sign “+” means the electrodes were further calendered prior to the measurements.

Electrode	Composition	Thickness (μm)	Porosity
AA005 (anode)	Graphite 91.83 wt%, Carbon 2 wt%, Binder 6 wt%, Oxalic Acid 0.17 wt%	48	35.1%
R2+A (anode)	Graphite 91.83 wt%, Carbon 2 wt%, Binder 6 wt%, Oxalic Acid 0.17 wt%	64	34.9%
R2-A (anode)	Graphite 91.83 wt%, Carbon 2 wt%, Binder 6 wt%, Oxalic Acid 0.17 wt%	78	38.2%
AC006 (cathode)	HE5050 92 wt%, Carbon 4 wt%, Binder 4 wt%	28	36.1%
R2+C (cathode)	NMC532 90 wt%, Carbon 5 wt%, Binder 5 wt%	65	32.6%
R2-C (cathode)	NMC532 90 wt%, Carbon 5 wt%, Binder 5 wt%	77	35.6%
HQ LCO (cathode)	LCO 93 wt%, Carbon 4 wt%, Binder 3 wt%	45	21.0%

Exhibit 2005

Ningde Ampere Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 3 of 13

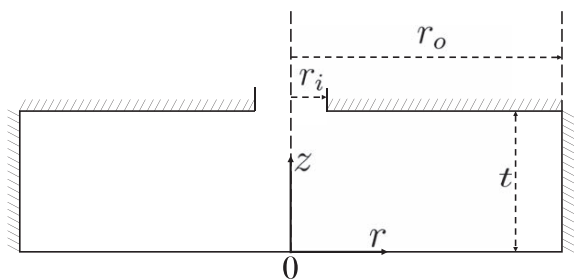


Figure 4. Schematic of the cylindrical model geometry and boundary conditions for the sample films or silver membrane in the probe.

Electrode cross-section analysis.—For R2+A, the impedance map was used to identify 2 locations of interest. The electrode was rinsed and dried. Then these two spots on the calendared anode film were milled using a broad ion beam (IB-19530CP JEOL cross-section polisher) for 4 h at an ion beam voltage of 5 kV. ThermoScientific Apreo C scanning electrode microscope (SEM) was used to demonstrate the particle and pore configuration of the milled cross-sections.

Average electronic conductivity measurement.—Electronic conductivity of the sample films was determined using a micro-flexible surface probe developed by Vogel et al.⁴¹ The technique can be considered an extension of 4-point probe methods and corrects for contact resistance between the probe and the sample film and for the presence of a metallic current collector. Averages were made from measurements at 400 locations to account for spatial variation.

Modeling

In order to obtain a MacMullin number from experimental data, an appropriate impedance model is needed. This section describes the derivation of a 2-dimensional transmission-line model (2D-TLM) using cylindrical coordinates. This model was then used, for both electrode samples and silver membranes, to invert impedance spectrum data and obtain local MacMullin numbers.

2D Transmission-line model.—The impedance model is similar to the 1-dimensional transmission-line model (1D-TLM) developed by Pouraghajan et al.³ However, for the local tortuosity measurement, a 2-dimensional transmission-line model (2D-TLM) using the cylindrical coordinate system is more suitable than the 1D-TLM. Figure 4 shows the geometry of the 2D-TLM. Because the electronic and ionic potentials are independent of the azimuth, the model only needs to be solved in 2 dimensions, r and z .

The governing equations for the conservation of electronic and ionic charge in the porous electrode are

$$0 = \sigma \left[\alpha \frac{\partial^2 \phi_1}{\partial r^2} + \frac{\alpha}{r} \frac{\partial \phi_1}{\partial r} + \frac{\partial^2 \phi_1}{\partial z^2} \right] + \frac{\phi_2 - \phi_1}{z_s} \quad [2]$$

$$0 = k \left[\alpha \frac{\partial^2 \phi_2}{\partial r^2} + \frac{\alpha}{r} \frac{\partial \phi_2}{\partial r} + \frac{\partial^2 \phi_2}{\partial z^2} \right] + \frac{\phi_1 - \phi_2}{z_s} \quad [3]$$

where ϕ_1 is the electronic potential, ϕ_2 is the ionic potential, σ is the electronic conductivity, k is the effective ionic conductivity, and z_s is the charge-transfer impedance between the electronic and ionic phases, and has units of $\Omega \text{ cm}^3$, meaning it is a volumetric impedance. The value of z_s , a complex number, is given by

$$z_s = \frac{1}{1/R_{ct} + Q_s(2\pi f)^{A_s}} \quad [4]$$

where R_{ct} is the Faradaic resistance, Q_s and A_s are constant phase element (CPE) parameters. f is the frequency of the alternating current, and j represents the imaginary part of a complex number. Even though the blocking-electrolyte is intended to eliminate Faradaic reaction,³ in practice some side reactions show a minor effect on the impedance measurement. Thus, including Faradaic resistance in the model helps data analysis. Additionally, α is an anisotropy factor that takes into account the difference in ionic transport in the r and z directions.⁴² In order to make the system of equations solvable, the same anisotropy factor is included in both the electronic and ionic governing equations, which may not be

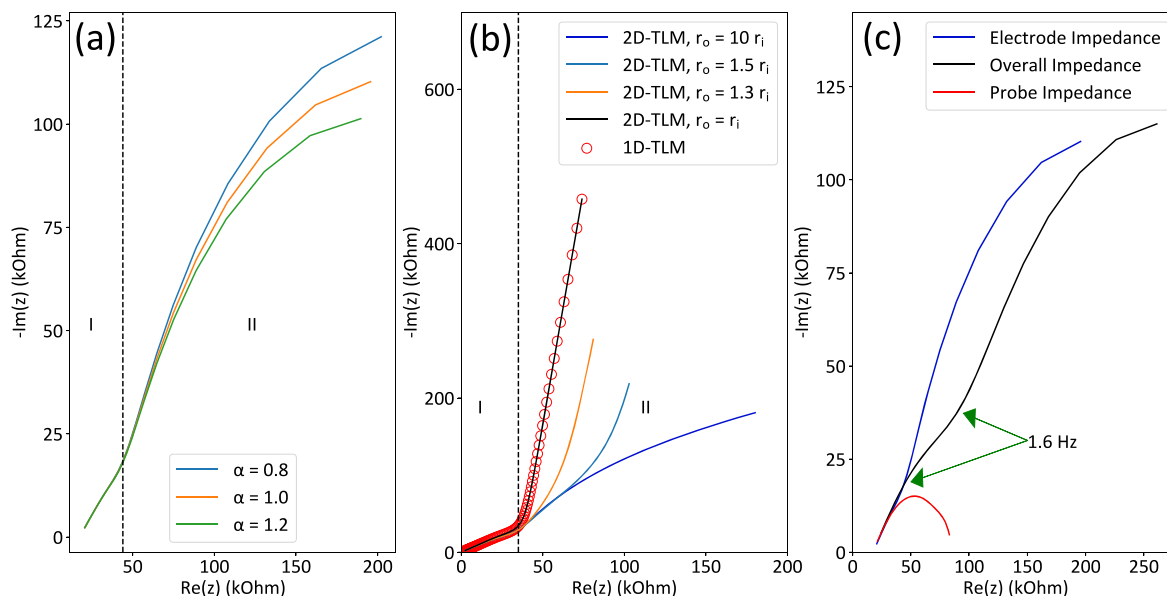


Figure 5. Representative Nyquist plots of models from 0.3 Hz to 4 kHz frequency. The vertical dashed lines separate region I and region II discussed in the text. (a) 2D-TLM with three different anisotropic factors (α). If $\alpha = 1$, the porous media is isotropic. If $\alpha > 1$, the tortuosity in r -direction is lower than that in z -direction, and vice-versa. (b) 1D-TLM compared to 2D-TLM with different geometries. (c) The electrode impedance, the probe impedance, and the overall impedance of a baseline case. To improve readability, the electrode and probe impedances are offset horizontally by the aperture resistance to align with the overall case. The green arrows point to the “elbow points” on the Nyquist plots as explained in the text.

accurate. However, in so far as $\sigma \gg k$, this assumption does not affect the model.

The equations for electronic (i_1) and ionic (i_2) current densities are:

$$i_1 = -\sigma \left[\alpha \frac{\partial \phi_1}{\partial r} \right] \quad [5]$$

$$i_2 = -k \left[\alpha \frac{\partial \phi_2}{\partial r} \right] \quad [6]$$

Figure 4 shows the geometry and the boundaries of the model. At $r = 0$, the derivatives of the potentials are zero in the r direction

$$\frac{\partial \phi_1}{\partial r} = 0, \quad \frac{\partial \phi_2}{\partial r} = 0 \quad [7]$$

At $r = r_o$, the potential gradient is zero due to the insulating boundary

$$\frac{\partial \phi_1}{\partial r} = 0, \quad \frac{\partial \phi_2}{\partial r} = 0 \quad [8]$$

In the case of electrode sample, a large value is chosen for r_o (i.e. $r_o > 5r_i$) such that it approximates macroscopic distances. At the current collector ($z = 0$), the normal ionic current density is assumed to be zero, and the electronic contact resistance between the current collector and electrode is assumed to be negligible, meaning the solid-phase potential is fixed at the current collector. The electronic potential at the current collector is set to 0 V.

$$\phi_1 = 0 \quad [9]$$

$$i_2 = -k \left(\frac{\partial \phi_2}{\partial z} \right) = 0 \quad [10]$$

A more detailed model was developed which included contact resistance, but, for the electrodes included in this work, it was found that contact resistance effects were negligible. At the top of electrode ($z = t$), there is no normal electronic current.

$$i_1 = -\sigma \left(\frac{\partial \phi_1}{\partial z} \right) = 0 \quad [11]$$

However, at the region contacting the aperture of the instrument, the normal ionic current density is given by

$$i_2 = -k \left(\frac{\partial \phi_2}{\partial z} \right) = \begin{cases} 0 & \text{for } r > r_i \\ G & \text{for } r < r_i \end{cases} \quad [12]$$

where r_i is the radius of the probe aperture and G is an arbitrary constant current density value. To increase the calculation speed of the model, the current density at the aperture ($z = t$, $r < r_i$) is assumed to be a constant value, namely G . Such an assumption does not reflect the real current distribution. However, compared with a numerical solution by COMSOL Multiphysics, where a more realistic current distribution is imposed on the boundary, the analytical model with imperfect assumption has only a small (<2%) error when estimating the MacMullin number of an electrode.

By solving this system of differential equations analytically, we obtain the potential of solid $\phi_1(r, z)$ and the potential of electrolyte $\phi_2(r, z)$ across the electrode (from the current collector to the aperture boundary) expressed as a series expansion:

$$\phi_1(r, z) = \sum_{n=0}^{\infty} J_0(\Psi_n r) \left[A_n \cosh(\lambda_n z) + B_n \sinh(\lambda_n z) + \frac{C_n}{\sigma} \cosh(\beta_n z) + \frac{D_n}{\sigma} \sinh(\beta_n z) \right] \quad [13]$$

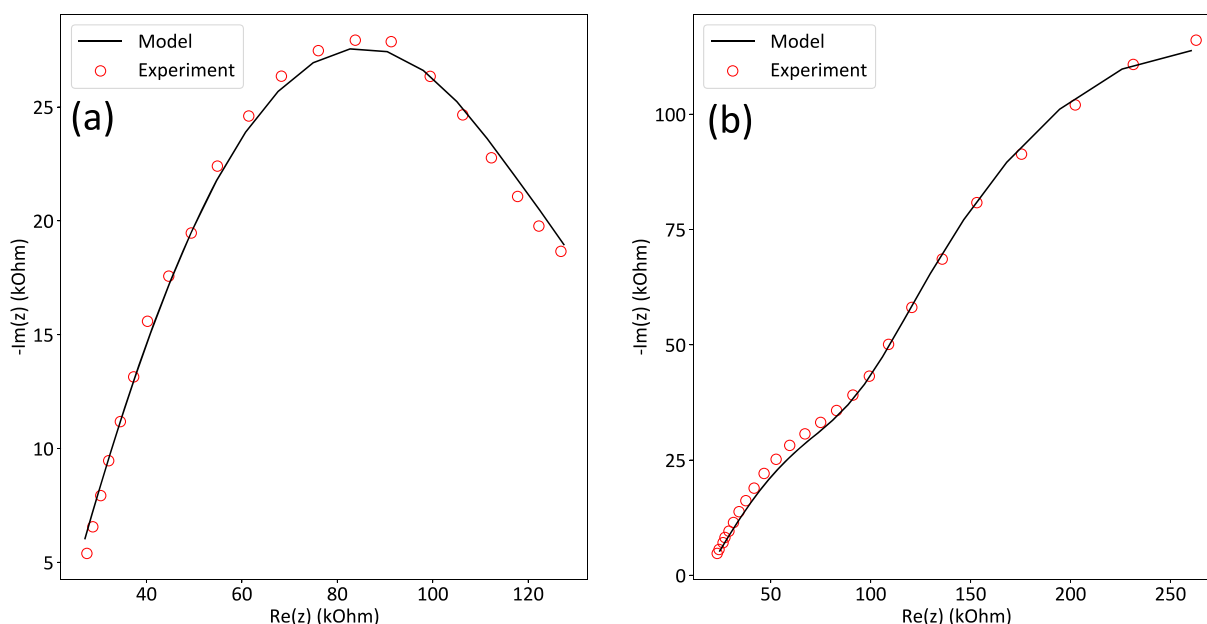


Figure 6. (a) The model fit and the experiment of a probe calibration test. (b) The model fit and the experiment of an electrode measurement. The Nyquist plots cover the frequency spectrum from 4 kHz (left of the plot) to 0.3 Hz (right of the plot).

$$\phi_2(r, z) = \sum_{n=0}^{\infty} J_0(\Psi_n r) \left[A_n \cosh(\lambda_n z) + B_n \sinh(\lambda_n z) - \frac{C_n}{k} \cosh(\beta_n z) - \frac{D_n}{k} \sinh(\beta_n z) \right] \quad [14]$$

where

$$\Psi_n = \frac{U_{1,n}}{r_o} \quad [15]$$

$$\lambda_n = \Psi_n \sqrt{\alpha} \quad [16]$$

$$\beta_n = \sqrt{\lambda_n^2 + \frac{\sigma + k}{\sigma k z_s}} \quad [17]$$

$U_{1,n}$ is the n^{th} root when $J_1(U_{1,n}) = 0$. J_1 is the Bessel function of type 1 and order 1, and J_0 is the Bessel function of type 1 and order 0. A_n , B_n , C_n , and D_n are spectral coefficients that can be determined by applying boundary conditions and solving the system of equations below

$$0 = A_n + \frac{C_n}{\sigma} \quad [18]$$

$$0 = B_n \lambda_n - \frac{D_n \beta_n}{k} \quad [19]$$

$$0 = A_n \lambda_n \sinh(\lambda_n t) + B_n \lambda_n \cosh(\lambda_n t) + \frac{C_n}{\sigma} \beta_n \sinh(\beta_n t) + \frac{D_n}{\sigma} \beta_n \cosh(\beta_n t) \quad [20]$$

$$\frac{r_i J_1(\Psi_n r_i)}{-\Psi_n k} = \frac{1}{2} r_o^2 J_0^2(\Psi_n r_o) \left[A_n \lambda_n \sinh(\lambda_n t) + B_n \lambda_n \cosh(\lambda_n t) - \frac{C_n}{k} \beta_n \sinh(\beta_n t) - \frac{D_n}{k} \beta_n \cosh(\beta_n t) \right] \quad [21]$$

The impedance Z is obtained as

$$Z = \frac{V_{\text{aperture}} - 0}{I} \quad [22]$$

where V_{aperture} is found by taking the average value of ϕ_2 at $z = t$ and $r < r_i$, and I is found by integrating the total ionic current across the aperture. 0 is chosen as the electrical potential at $z = 0$. V_{aperture} and I are calculated as follows

$$V_{\text{aperture}} = \frac{1}{\pi r_i^2} \int_0^{r_i} \phi_2(r, t) 2\pi r dr \quad [23]$$

$$I = \pi r_i^2 G \quad [24]$$

The total impedance of the electrode can be expressed as the following series expansion:

$$Z = \frac{2}{\pi r_i^3 k} \sum_{n=0}^{\infty} \frac{J_1(\Psi_n r_i)}{\Psi_n} \left[A_n \cosh(\lambda_n t) + B_n \sinh(\lambda_n t) - \frac{C_n}{k} \cosh(\beta_n t) - \frac{D_n}{k} \sinh(\beta_n t) \right] \quad [25]$$

In the above expressions for Z , note that G cancels out and does not appear.

All the data in this study are analyzed using the complete model above (Eq. 25). However, to reduce the computation cost and

increase the speed of data analysis, the model can be greatly simplified by assuming a large electronic conductivity in the sample and silver membrane. In the limit that $\sigma \gg k$, the electronic potential in the electrode becomes constant ($\phi_1 = 0$). The following simplified model was found to be satisfactory for the electrodes studied here.

$$Z = \frac{4}{\pi k r_i^2 r_o^2} \sum_{n=0}^{\infty} \frac{J_1^2(\Psi_n r_i)}{\Psi_n^2 J_0^2(\Psi_n r_o) \beta_n \tanh(\beta_n t)} \quad [26]$$

where

$$\Psi_n = \frac{U_{1,n}}{r_o} \quad [27]$$

$$\lambda_n = \Psi_n \sqrt{\alpha} \quad [28]$$

$$\beta_n = \sqrt{\lambda_n^2 + \frac{1}{k z_s}} \quad [29]$$

In practical application, the sum of Eqs. 25 and 26 is truncated at 200 terms.

Nyquist plot illustration.—Understanding the physical meaning of the Nyquist plot of the model is important for the data inversion process. Figure 5a shows representative Nyquist plots of the solution (Eq. 25) with different anisotropy factor values. The Nyquist plots can be divided into two regions. Region I, for which frequencies are large, represents the ionic current confined to the region directly below the aperture. The impedance of region I is the ionic impedance in the z -direction. Region II, which is for low frequencies, indicates current flow that spreads out laterally (in r -direction) and thus is more sensitive to the anisotropy factor (α). To a lesser degree, and generally at even lower frequencies, region II is also influenced by any Faradaic reaction. The elbow point between region I and region II thus represents the frequency at which the current path starts expanding laterally.

To further demonstrate the ionic current expansion discussed above and to validate the computation outcome of the model, the 2-D transmission-line model (2D-TLM) is compared with the 1-D transmission-line model (1D-TLM). It is worth noting that region II of 1D-TLM, which is a straight vertical line in case of blocking-electrolyte, strictly represents the large but non-infinite Faradaic resistance, instead of lateral current expansion. By increasing the value of the inner radius (r_i) toward the outer radius (r_o), the 2D-TLM behaves more like a 1D-TLM. As shown in Fig. 5b, when r_i is increased, region II of the 2D-TLM becomes more vertical, which means Faradaic resistance is emphasized over lateral current expansion. When $r_o = r_i$, the lateral current expansion is eliminated in 2D-TLM, and the 2D-TLM converges to the 1D-TLM.

The impedance of both electrode and the probe that consists of 10 layers of silver membrane can be expressed by Eqs. 25 and 26. Figure 5c shows the relative contribution to the overall impedance of a baseline case from the probe and the electrode sample. The probe impedance is relatively small though non-negligible. The upper green arrow shows the elbow point on the overall impedance. The lower green arrow shows the same on the electrode impedance. A key feature of the probe impedance is that it preserves and does not obscure the elbow point (see Ref. 3). In this instance, the elbow points happen at the same frequency (1.6 Hz) on both Nyquist plots, which means that probe impedance does not disturb the process of estimating the MacMullin number of electrodes.

Impedance model of experiment system.—The 2D transmission-line model developed above represents only the impedance in the porous media. However, as shown in Fig. 5c and Eq. 30, the overall impedance consists of the electrode impedance, the probe impedance

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 6 of 13

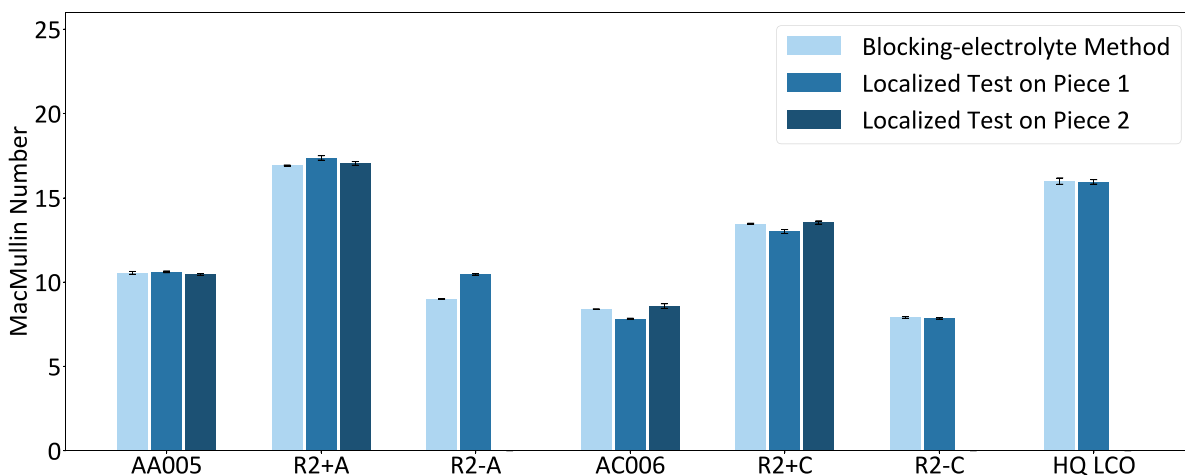


Figure 7. Comparison between the benchmark MacMullin numbers from the pouch cell measurements and the average MacMullin numbers from the local tortuosity measurements (1 mm scan). The error bars represent the 95% confidence interval of repeated measurements.

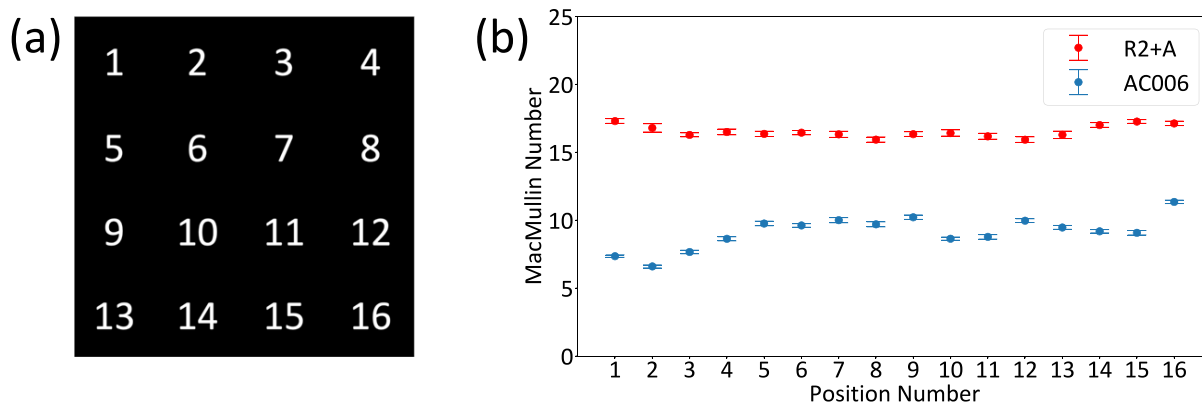


Figure 8. (a) Relative sampling locations on each electrode film. The grid spacing is 2 mm. (b) MacMullin numbers and 95% confidence intervals at grid locations for R2+A (top series) and for AC006 (bottom series).

(i.e. the silver membrane layers), and the resistance of the aperture:

$$Z_{\text{Overall}} = Z_{\text{Probe}} + Z_{\text{Aperture}} + Z_{\text{Electrode}} \quad [30]$$

The form of the 2D-TLM solution (Eq. 25 or 26 in this study) is used for both Z_{Probe} and $Z_{\text{Electrode}}$. The value of Z_{Aperture} is calculated from

$$Z_{\text{Aperture}} = \frac{t_f}{k_{\text{int}} \pi r_i^2} \quad [31]$$

where t_f is the thickness of the aperture, and r_i is its radius. To isolate $Z_{\text{Electrode}}$, Z_{Probe} was calibrated during the experiments.

Impedance data inversion.—Each impedance spectrum was inverted into a MacMullin number through a least squares fit, by varying five parameters (MacMullin number, Faradaic resistance, constant phase element (CPE) parameters, and anisotropy factor) to minimize the objective function

$$F = \sum_{n=1} \frac{(|Z_{\text{Exp}} - Z_{\text{Overall}}|)^2}{|Z_{\text{Exp}}|^2} \quad [32]$$

where Z_{Exp} is the experimental impedance at a particular frequency. In this study, each regression between model and experiment includes 25 data points with frequency values that follow logarithmic distribution from 0.3 Hz to 4 kHz.

In case of probe calibration, the properties of the probe can be obtained by a least squares fit, using the objective function (Eq. 32), where $Z_{\text{Electrode}} = Z_{\text{Probe}}$, meaning a symmetric geometry where a 10-layer silver membrane stack is located on both sides of the aperture. As shown in Fig. 6a, the model satisfactorily fit the experimental data, with in this case a root mean square relative error of about $3 \cdot 10^{-6}$, meaning that the parameters of the probe are accurately calibrated. The MacMullin number of the silver membrane is approximately 3.

After determining the probe impedance and the ionic resistance of the aperture, the MacMullin number of the electrode can be obtained through least squares fit, using Eq. 32. Figure 6b shows for a representative case that the overall impedance model and the experiment data have a satisfactory fit.

We observed some confounding between parameters in the regression model, meaning results were sensitive to guess values in some cases. To minimize this effect, 12 different sets of model parameter guess values were used for each experimental Nyquist plot, meaning the regression was repeated 12 times. The final parameter values were obtained by calculating a weighted average of the best fit parameters obtained from different starting points according to

$$P_{\text{final}} = \frac{\sum_{i=1}^{12} w_i P_i}{\sum_{i=1}^{12} w_i} \quad [33]$$

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 7 of 13

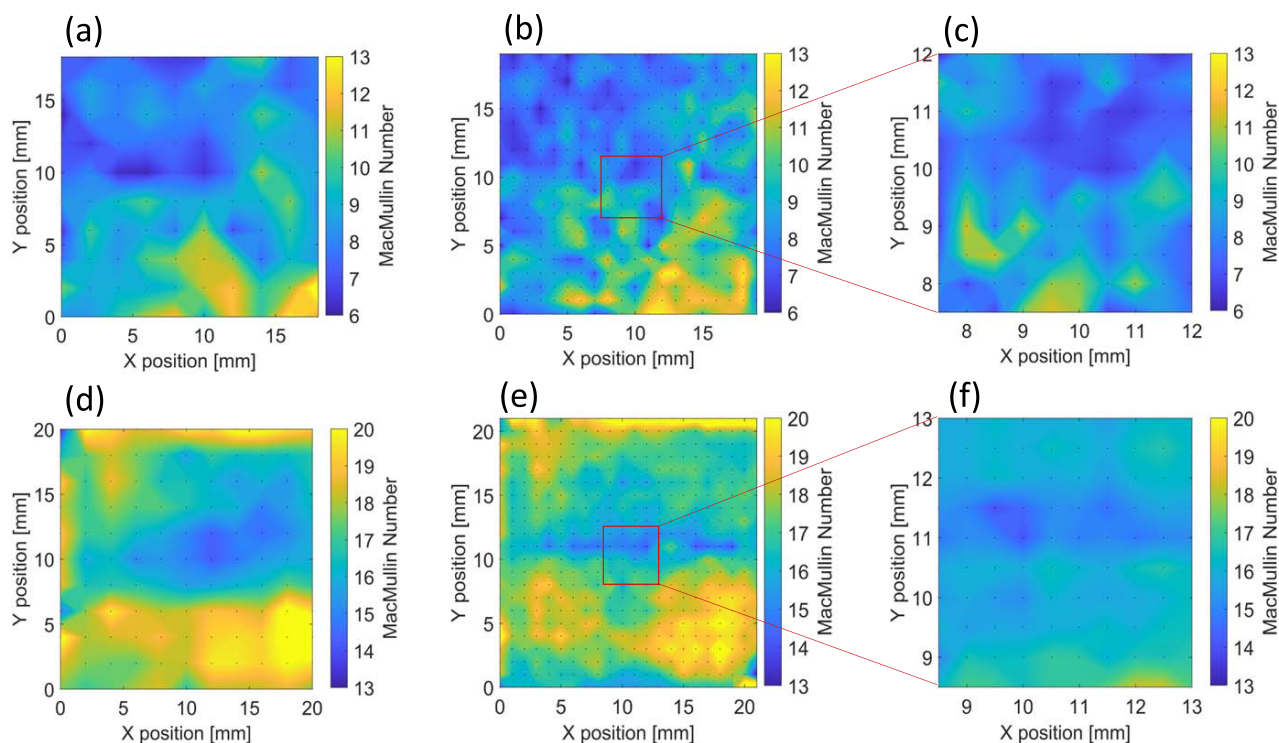


Figure 9. Contour maps of MacMullin numbers for AC006 (a)–(c) and for R2+A (d)–(f). The two maps in the left ((a) and (d)) are from the 2 mm scan. The two maps in the middle ((b) and (e)) are from the 1 mm scan. The two maps in the right ((c) and (f)) are from the 0.5 mm scan in the middle of the electrodes (in the red square of part (b) and part (e)). The dots on the plots represent the location where the data were collected.

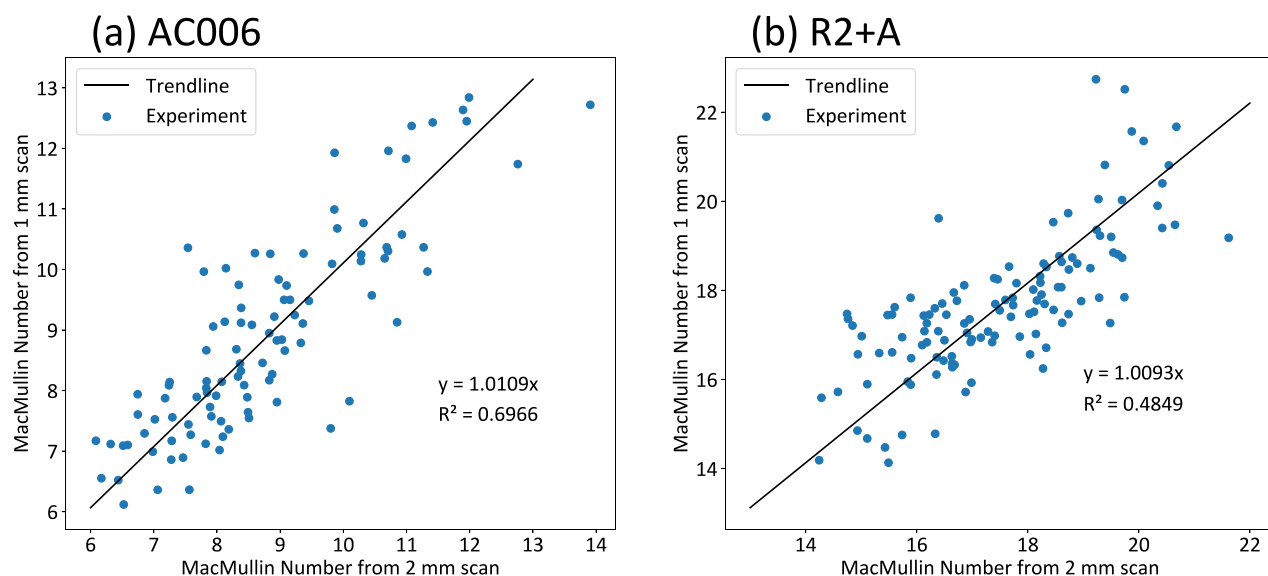


Figure 10. Parity plots based on the MacMullin number values collected from repeated electrode scans for (a) AC006 and for (b) R2+A.

where p_i is the value of certain parameter from regression i , p_{final} is the ultimate value of the parameter after computing weighted average, and w_i is the weight from each regression:

$$w_i = \exp\left(-2\frac{F_i}{F_{\min}}\right) \quad [34]$$

F_i is the sum of squared error, defined by Eq. 32, for regression i , $F_{\min}$ is the smallest value of F_i among these 12 regressions. The

particular form of Eq. 34 was determined empirically and serves to give greater weight to the parameter values that yield the smallest error.

Results and Discussion

Validation of experiment technique.—To establish that the aperture probe can distinguish between and accurately measure the tortuosity of different electrodes, we compare the mean value of

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 8 of 13

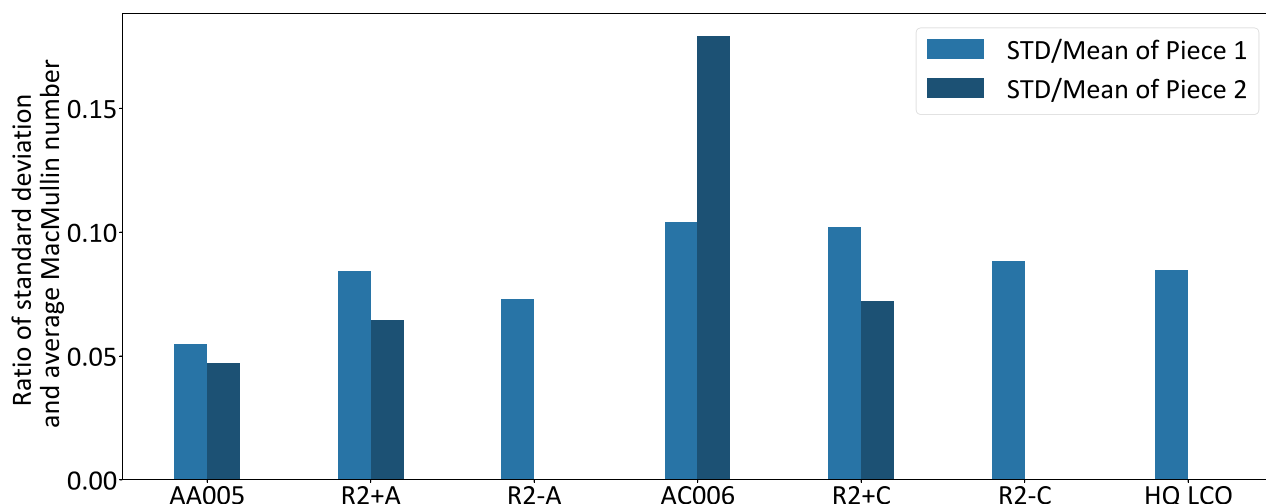


Figure 11. The ratio of standard deviation (from 1 mm scan) to average MacMullin number (from 1 mm scan) of each electrode measured in this research.

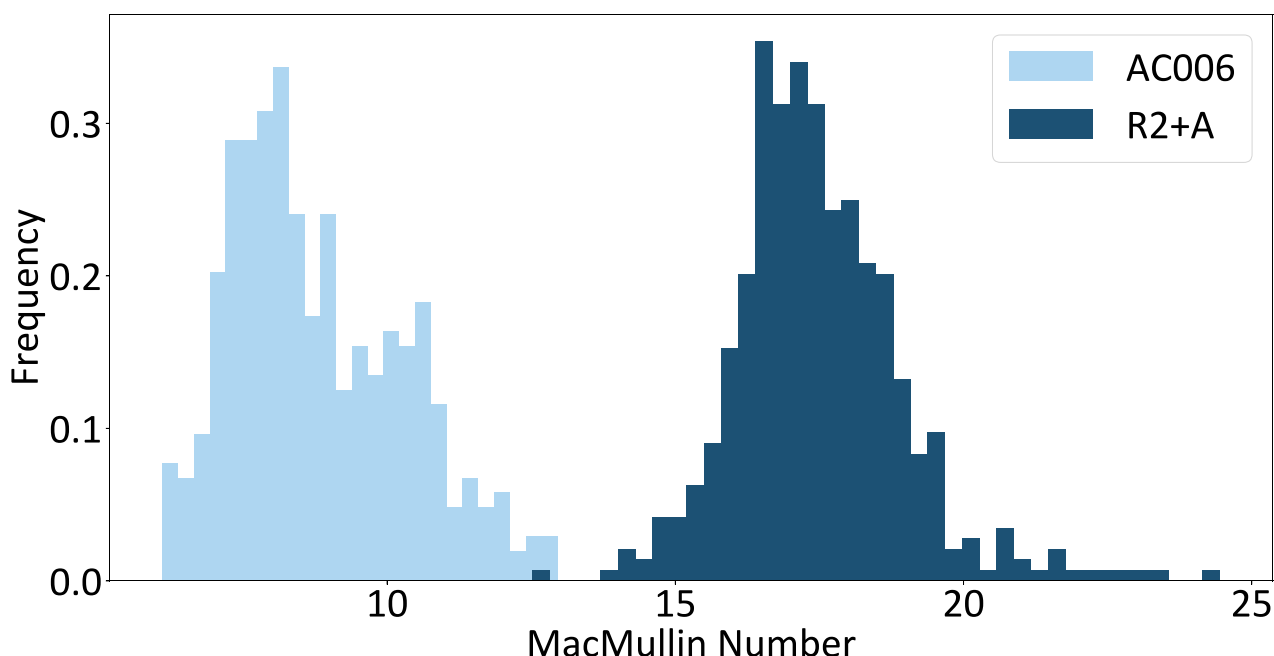


Figure 12. Frequency distribution of the MacMullin numbers from 1 mm scan for AC006 and R2+A.

local MacMullin number and the benchmark MacMullin number obtained from pouch cell measurements. We used the aperture probe to measure the local MacMullin numbers of 7 electrodes by scanning with 1 mm spacing between each grid point. The total number of locations tested was about 400 on each electrode, except for R2-A and R2-C that had 1440 measured locations. Because local MacMullin numbers are equivalent to resistances of ionic transport in a parallel configuration, the average MacMullin number of each piece of electrode was obtained by calculating the harmonic mean of all the local MacMullin numbers.

Benchmark values and the average local values for the MacMullin number are shown side by side in Fig. 7. The results show reasonable agreement between the two methods considering the differences in data collection between the two methods. After conducting a pooled 2 sample t-test, we found out that all of the samples, except for AC006 Piece 1 and R2-A, have a statistical agreement between the two measurement methods at a 95%

confidence interval. The results show that the aperture probe can detect the difference between electrodes in terms of MacMullin number and estimate the average MacMullin number of the electrodes.

In our experience, cathodes do not usually have a higher MacMullin number than anodes. However, due to the relative porosities of the electrodes in our data set, HQ LCO and R2+C showed MacMullin numbers larger than AA005 and R2-A.

Verification of repeatability of measurements.—Two electrodes, piece 2 of AC006 and piece 1 of R2+A (in the following discussion, “AC006” and “R2+A” will be used to specifically refer to these two pieces of electrode), were chosen to conduct further investigations because these two electrodes have compositions of commercial and research interest.

To verify the repeatability of the aperture probe measurements, we used the probe to scan a 4 by 4 grid of points in the middle of

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 9 of 13

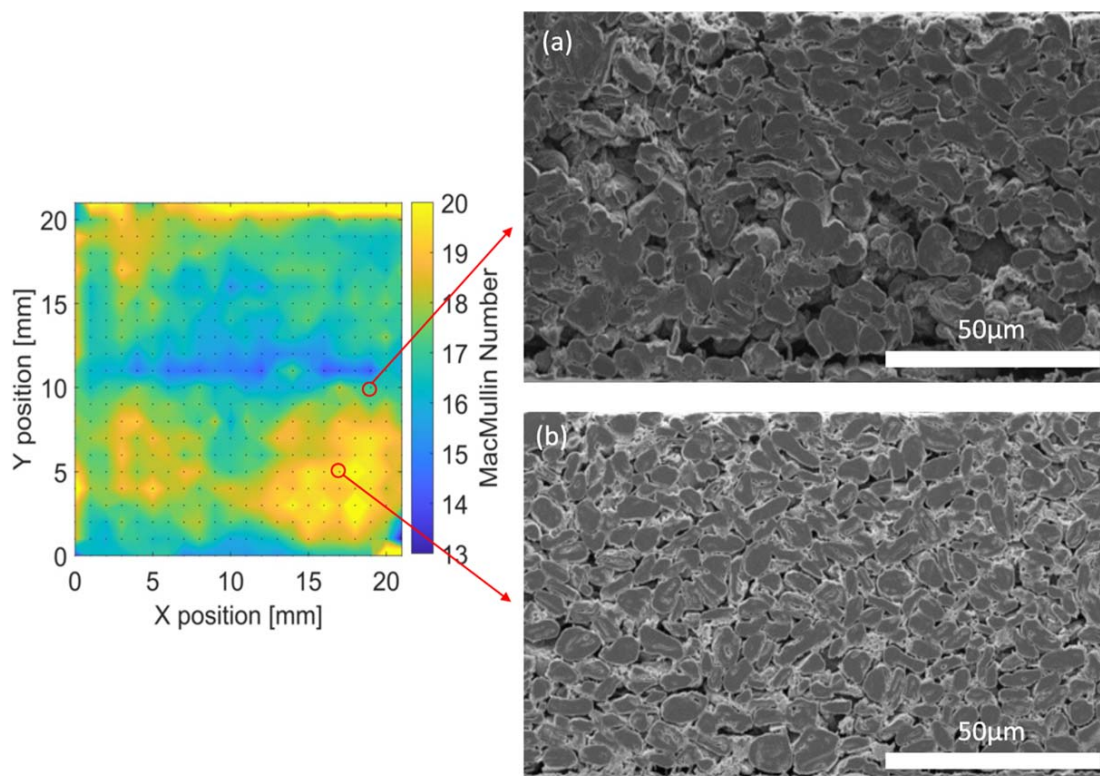


Figure 13. SEM images (right) of the cross-section of R2+A from two different locations indicated in the contour map (left).

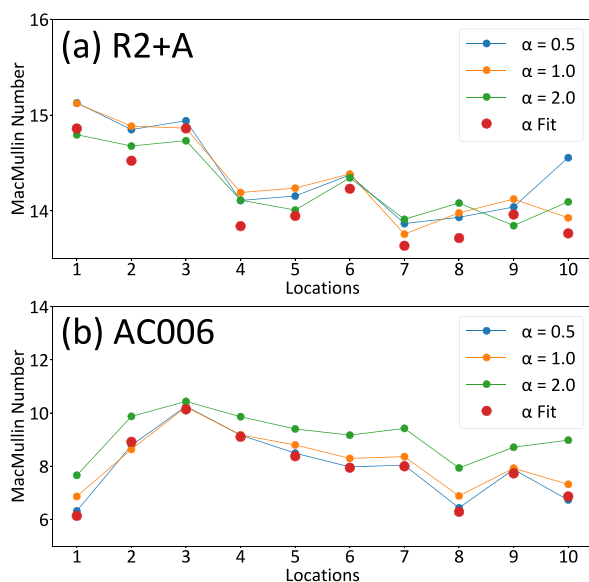


Figure 14. MacMullin number values inverted from 10 impedance spectra of R2+A and AC006 for different assumed anisotropy values (α) and for when anisotropy value acts as a fitting parameter that varies, dependent on locations, from 1.4 to 2.1 for R2+A and from 0.16 to 0.86 for AC006. Lines between points are to guide eye.

AC006 and R2+A with 2 mm spacing between each point (see Fig. 8a). This 16-point scan was repeated 20 times for each electrode, meaning that each location was sampled 20 times. The average MacMullin numbers of repeated locations, together with the 95% confidence intervals, are displayed in Fig. 8b.

It is clear from Fig. 8b that the uncertainty of the aperture probe measurements and the uncertainty of the data inversion are, in general, less than the variation from one location to another on the electrode. This implies that seemingly anomalous conductivity at some locations, such as at position 16 for AC006 and at position 1 for R2+A must be due to a material difference at that location because the repeated (descend and lift off) measurements at that location are consistent and do not exhibit greater-than-expected variation. For both AC006 and R2+A, the confidence intervals of each tested location are similar to each other (about 0.1 to 0.2). The area tested on AC006 has a higher spatial variation of MacMullin number than that on R2+A.

Additional tests were done to check for repeatability. We re-scanned AC006 and R2+A, with grid spacing 2 mm and then, for a smaller region in the center, with grid spacing 0.5 mm. Figure 9 compares side-by-side the resulting 2-mm, 1-mm, and 0.5-mm maps. For each electrode, by comparing the 1-mm map with the 2-mm map, a similar pattern of MacMullin number distribution can be identified. For example, the high-MacMullin number region on the lower-right of R2+A is displayed in both maps.

The 0.5-mm maps were generated to further investigate the spatial variation of MacMullin number. Part (c) of Fig. 9 shows that, for AC006, by increasing the resolution of the scan, more spatial variation can be revealed. However, increasing the resolution of electrode scan does not reveal more detailed spatial variation for R2+A (see part (f) of Fig. 9), suggesting that R2+A has a larger size scale for heterogeneity in MacMullin number than AC006 does. Comparing part (b) with part (e) in Fig. 9, R2+A further shows a larger length scale of MacMullin number variation than for AC006. It is also worth-noting that the probe has a resolution limitation of (400 μm), and an electrode scan with resolution lower than 400 μm will not reveal further detail. Therefore, a smaller aperture size may be required according to the research need.

To quantitatively validate the repeatability of the aperture probe, we generated parity plots (Fig. 10) for each electrode to compare the

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 10 of 13

Table III. Pearson correlation coefficients between MacMullin number and other fitting parameters. For a characteristic location on AC006

Parameter pair	R^2
N_m, Q_s	$7.43 \cdot 10^{-3}$
N_m, A_s	$1.15 \cdot 10^{-1}$
N_m, R_{ct}	$-7.55 \cdot 10^{-2}$
N_m, α	$-6.75 \cdot 10^{-2}$

MacMullin numbers at the corresponding locations from the 2 mm scan and the 1 mm scan. As shown, the MacMullin numbers from the two repeated measurements have linear correlation coefficients (i.e. R^2) that suggest a mix of repeatability and noise. One of the possible reasons for reduced repeatability is slight positional inaccuracy (i.e. offset) from one scan to the next due to the relatively large scanned areas.

Battery electrode heterogeneity study.—The degree of heterogeneity of battery electrodes is of great interest to understand the causes of lithium plating. We used the ratio of the standard deviation to the average MacMullin number to quantify heterogeneity of a given electrode and length scale of sampling.

Figure 11 shows that the ratio varies significantly from one electrode to the other, suggesting that under the same length scale, the degree of heterogeneity is different from one electrode to the other. Even though the two pieces of AC006 had similar average MacMullin numbers (Fig. 7), they have substantially different heterogeneity metrics (Fig. 11).

Another approach to study electrode heterogeneity is through frequency distribution in terms of MacMullin number. Figure 12 shows two frequency distribution plots of MacMullin numbers for AC006 and R2+A. As shown, R2+A has a longer tail toward higher MacMullin number, which suggests that there are some spots on R2+A that have substantially higher MacMullin number and therefore poor ionic access. Spots that have higher MacMullin numbers should have a higher tendency for plating, though future work is needed to determine the correlation between the MacMullin number and local lithium plating.

Appendix shows the MacMullin number maps of the other samples tested in this study. The average, frequency distribution, and heterogeneity length scale of each electrode can be observed from these maps.

MacMullin number and morphology of electrode.—To verify the correlation between the MacMullin number and the morphology of the electrode, two SEM images of the cross-section of R2+A from different locations are shown in Fig. 13. The cross-section at the location with low MacMullin number (part (a)) has larger pore sizes and a clear percolation passing across the thickness of the electrode. The pores at the high MacMullin number location (part (b)) are smaller with a less-obvious percolation pathway observed at that location. Therefore, the particle-level morphology of the electrode confirms the variable ionic transport. Observed by means of the aperture probe, heterogeneity cannot be observed through the naked eye.

Effect of anisotropy on data inversion.—Anisotropy describes properties that depend on spatial orientation. The existence of anisotropy in electrodes has been observed by Ebner et al.⁴² As is explained in the previous section, an anisotropy factor (α) is included in the 2D-TLM to describe the difference between vertical MacMullin number and lateral MacMullin number and to help with the curve fit at the low-frequency region, which is the region II in Fig. 5a.

Even though the scope of this study focuses on vertical MacMullin number as the more relevant parameter for cell

performance, and the degree of anisotropy is not fully understood yet, the aperture probe can still give an indication of anisotropy. For example, for R2+A, the anisotropy values obtained from data inversion are usually larger than one, which means that the lateral tortuosity is probably lower than vertical tortuosity. For AC006, the anisotropy values obtained from data inversion are usually lower than one, which means that the lateral tortuosity is probably higher than vertical tortuosity.

It is also interesting to examine if the anisotropy parameter (α) confounds with other parameters, especially the vertical MacMullin number. As shown in Fig. 14, by constraining the anisotropy factor to a particular value, the resulting fitted average MacMullin number is slightly changed, but the relative order of MacMullin number between pairs of locations is not altered. Also shown in the figure are the results for a full fit in which α is not constrained. This result suggests that some uncertainty in anisotropy factor does not substantially change the pattern of MacMullin number map for electrodes.

To summarize, the localized ionic conductivity measurement method is modestly sensitive to anisotropy. Whether this method can be used to accurately determine anisotropy requires further investigation.

Correlations between fitting parameters.—To make sure that the MacMullin number does not confound with other fitting parameters, Pearson correlation coefficients between MacMullin number and other fitting parameters were calculated with the same weighting scheme as previously discussed, one such result is shown for a characteristic location on AC006 in Table III. It shows that the correlation between MacMullin number and other fitting parameters is negligible (between -0.3 and 0.3), which means that the MacMullin number can be determined relatively independently. Compared to the average value for this location (6.46), the variance of MacMullin number was small ($4.19 \cdot 10^{-5}$), which means the MacMullin number was well-converged.

Comparison between the complex and simplified model.—In this study, all the experiment data were analyzed using the complete model (Eq. 25). However, to accelerate data processing, the simplified model (Eq. 26) is recommended. For our Python code, the speed-up factor was around 10. The simplified model is based on the assumption that $\sigma \gg k$, and when $\sigma > 10k$, the two models generated essentially the same impedance plot for the cases tested here. To compare the outcome of data analysis of these two models, we used these two models to separately analyze 100 experiment data files of AC006. The electrolyte used for experiments has a conductivity of about $500 \mu\text{S cm}^{-1}$, and AC006 has electronic conductivity on average 25 mS cm^{-1} , which is 50 times higher than that of electrolyte. The two models yielded average MacMullin numbers with less than 2% difference, meaning that the simplified model generates an error smaller than the uncertainty given in Fig. 7. As for anodes, the electronic conductivity is about 1000 to 3000 mS cm^{-1} , which is 5000 times higher than the conductivity of electrolyte, so the simplified model is also widely applicable to the anodes.

Conclusions

An aperture probe for measuring localized ionic transport has been designed, fabricated, and tested. An automated fixture coupled with robust measurement protocols allows accurate, repeatable measurements to be taken. The ability of the aperture probe, when combined with a 2-dimensional transmission-line model to quantify the MacMullin number, has been validated through comparison with previously developed techniques.³

The local MacMullin numbers of five commercial-quality electrodes were measured and spatially characterized using the aperture probe. These results confirm that significant heterogeneity of MacMullin number exists in the electrodes, and that the degree of

Exhibit 2005

Ningde Amperex Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 11 of 13

heterogeneity varies from one electrode to the other. Electrodes with a more drastic variation in MacMullin number need to be scanned with higher resolution in order to better understand those systems. In future work, the size of the aperture could be adapted as needed for this and other applications.

The local MacMullin number measurement technique will be of aid to battery manufacturers and researchers to better identify and remedy sources of heterogeneity and electrode quality control issues that are not obvious with other techniques.

A planned avenue for future exploration is to compare localized ionic transport with localized electronic transport⁴¹ or other properties such as state of charge or state of health.

Acknowledgments

Funding was provided from the Vehicle Technologies Office of the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy under the guidance of the Advanced Battery Cell Research Program (eXtreme fast charge Cell Evaluation of Lithium-ion batteries, XCEL).

Appendix: Contour Maps of the Electrodes

The contour plots of MacMullin number of all the electrodes, other than AC006 Piece 2 and R2+A Piece 1 (previously discussed in detail), are displayed in Fig. 15. The MacMullin numbers are

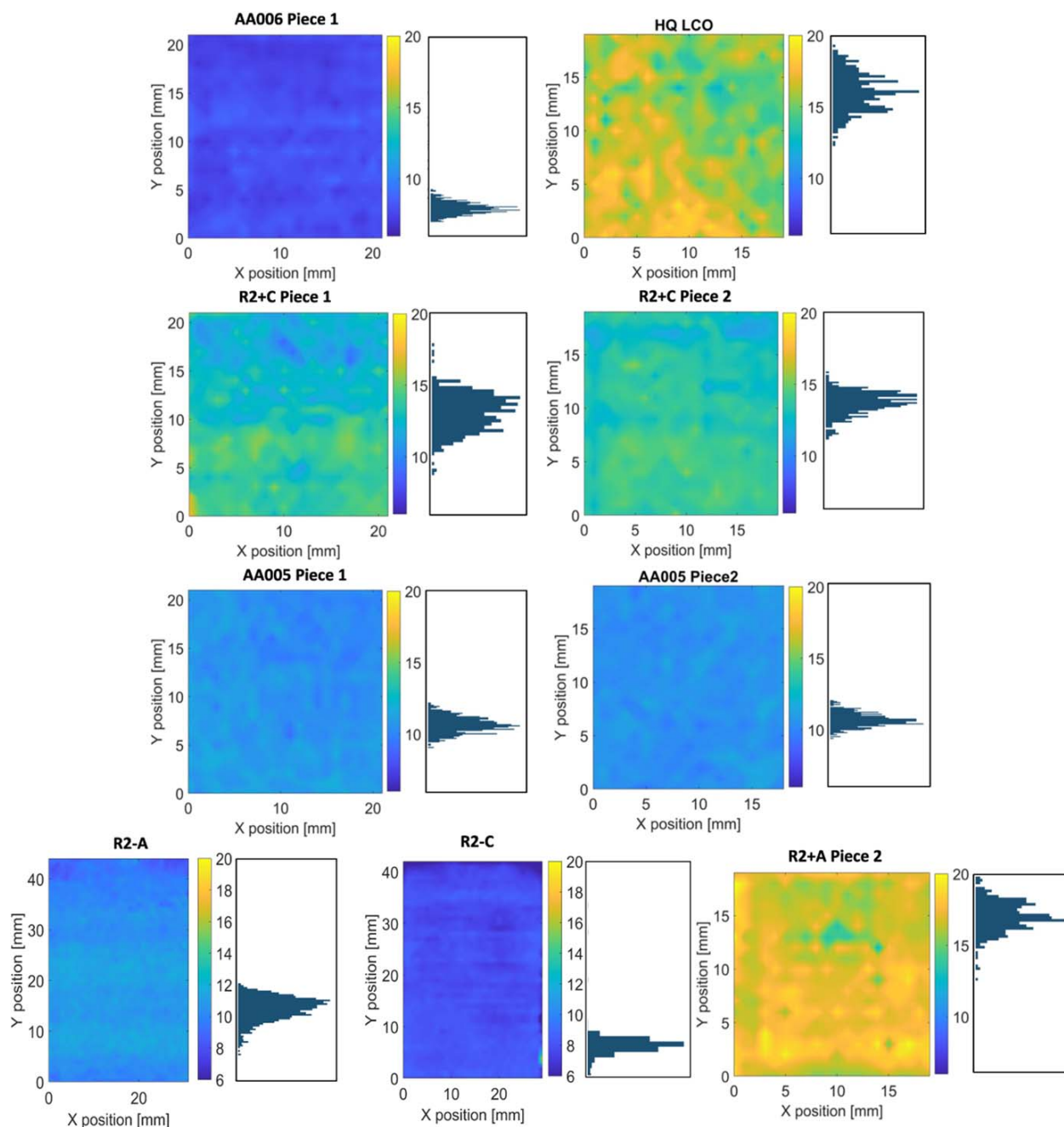


Figure 15. 1 mm scan maps (left) and frequency distribution plots (right) of several electrodes tested in this study. The MacMullin number scale is represented by color bars. The numbers beside the color bar are MacMullin numbers that mark both the color bars and the frequency distribution plots. The size of samples is reflected by the axis.

Exhibit 2005

Ningde Ampere Technology Ltd.

IPR2023-00587, U.S. Patent No. 10,964,987

Page 12 of 13

represented by the same color scale for all the electrodes so that the average MacMullin number can be estimated through the color. Each contour map is accompanied by a frequency distribution of MacMullin numbers to help visualize the heterogeneity.

ORCID

Baichuan Liu  <https://orcid.org/0000-0001-9231-1292>
 Mojdeh Nikpour  <https://orcid.org/0000-0001-6069-0611>
 Brian A. Mazzeo  <https://orcid.org/0000-0002-3558-1461>
 Dean R. Wheeler  <https://orcid.org/0000-0001-5017-3194>

References

1. T.-T. Nguyen, A. Demortière, B. Fleutot, B. Delobel, C. Delacourt, and S. J. Cooper, "The electrode tortuosity factor: why the conventional tortuosity factor is not well suited for quantifying transport in porous Li-ion battery electrodes and what to use instead." *npj Computational Materials*, **6**, 1 (2020).
2. I. V. Thorat, D. E. Stephenson, N. A. Zacharias, K. Zaghib, J. N. Harb, and D. R. Harb, "Quantifying tortuosity in porous Li-ion battery materials." *Journal of Power Sources*, **188**, 592 (2009).
3. F. Pouraghajan, H. Knight, M. Wray, B. Mazzeo, R. Subbaraman, J. Christensen, and D. Wheeler, "Quantifying tortuosity of porous Li-ion battery electrodes: Comparing polarization-interrupt and blocking-electrolyte methods." *J. Electrochem. Soc.*, **165**, A2644 (2018).
4. X. Jie, "How lithium dendrites form in liquid batteries." *Science*, **366**, 426 (2019).
5. P. R. Shearing, L. E. Howard, P. S. Jørgensen, N. P. Brandon, and S. J. Harris, "Characterization of the 3-dimensional microstructure of a graphite negative electrode from a Li-ion battery." *Electrochemistry communications*, **12**, 374 (2010).
6. F. Röder, S. Sonntag, D. Schröder, and U. Krewer, "Simulating the impact of particle size distribution on the performance of graphite electrodes in lithium-ion batteries." *Energy Technology*, **4**, 1588 (2016).
7. M. R. Kok, R. Jervis, D. Brett, P. R. Shearing, and J. T. Gostick, "Insights into the effect of structural heterogeneity in carbonized electrospun fibrous mats for flow battery electrodes by x-ray tomography." *Small*, **14**, 1703616 (2018).
8. A. N. Mistry and P. P. Mukherjee, "Analyzing the importance of particle morphology and heterogeneity in Li-ion battery electrodes." *ECS Meeting Abstracts* (IOP Publishing) p. 271 (2018).
9. P. Maire, A. Evans, H. Kaiser, W. Scheifele, and P. Novák, "Colorimetric determination of lithium content in electrodes of lithium-ion batteries." *J. Electrochem. Soc.*, **155**, A862 (2008).
10. H. Liu, S. Kazemianavi, A. Grenier, G. Vaughan, M. Di Michiel, B. J. Polzin, K. Thornton, K. W. Chapman, and P. J. Chupas, "Quantifying reaction and rate heterogeneity in battery electrodes in 3D through operando x-ray diffraction computed tomography." *ACS applied materials & interfaces*, **11**, 18386 (2019).
11. K. Chen et al., "Morphological effect on reaction distribution influenced by binder materials in composite electrodes for sheet-type all-solid-state lithium-ion batteries with the sulfide-based solid electrolyte." *The Journal of Physical Chemistry C*, **123**, 3292 (2019).
12. H. Jun and J. Zhang, "Theory of impedance response of porous electrodes: simplifications, inhomogeneities, non-stationarities and applications." *J. Electrochem. Soc.*, **163**, A1983 (2016).
13. M. M. Forouzan, B. A. Mazzeo, and D. R. Wheeler, "Modeling the effects of electrode microstructural heterogeneities on Li-ion battery performance and lifetime." *J. Electrochem. Soc.*, **165**, A2127 (2018).
14. S. J. Harris and P. Lu, "Effects of inhomogeneities? nanoscale to mesoscale? on the durability of Li-ion batteries." *The Journal of Physical Chemistry C*, **117**, 6481 (2013).
15. R. Gogoana, M. B. Pinson, M. Z. Bazant, and S. E. Sarma, "Internal resistance matching for parallel-connected lithium-ion cells and impacts on battery pack cycle life." *Journal of Power Sources*, **252**, 8 (2014).
16. F. Xu, B. Beak, and C. Jung, "In situ electrochemical studies for Li⁺ ions dissociation from the licoo 2 electrode by the substrate-generation/tip-collection mode in secm." *Journal of Solid State Electrochemistry*, **16**, 305 (2012).
17. Z. J. Barton and J. Rodríguez-López, "Lithium ion quantification using mercury amalgams as in situ electrochemical probes in nonaqueous media." *Anal. Chem.*, **86**, 10660 (2014).
18. Y. Takahashi et al., "Nanoscale visualization of redox activity at lithium-ion battery cathodes." *Nat. Commun.*, **5**, 1 (2014).
19. A. L. Lipson, R. S. Ginder, and M. C. Hersam, "Nanoscale in situ characterization of Li-ion battery electrochemistry via scanning ion conductance microscopy." *Adv. Mater.*, **23**, 5613 (2011).
20. N. Balke, S. Jesse, A. N. Morozovska, E. Eliseev, D. W. Chung, Y. Kim, L. Adamczyk, R. E. Garcia, N. Dudney, and S. V. Kalinin, "Nanoscale mapping of ion diffusion in a lithium-ion battery cathode." *Nat. Nanotechnol.*, **5**, 749 (2010).
21. G. Zampardi, E. Ventosa, F. L. Mantia, and W. Schuhmann, "In situ visualization of Li-ion intercalation and formation of the solid electrolyte interphase on TiO₂ based paste electrodes using scanning electrochemical microscopy." *Chem. Commun.*, **49**, 9347 (2013).
22. G. Zampardi, E. Ventosa, F. L. Mantia, and W. Schuhmann, "Scanning electrochemical microscopy applied to the investigation of lithium (de-) insertion in TiO₂." *Electroanalysis*, **27**, 1017 (2015).
23. G. Zampardi, S. Klink, V. Kuznetsov, T. Erichsen, A. Maljusch, F. L. Mantia, W. Schuhmann, and E. Ventosa, "Combined AFM/SECM investigation of the solid electrolyte interphase in Li-ion batteries." *ChemElectroChem*, **2**, 1607 (2015).
24. H. Bültel, F. Peters, J. Schwenzel, and G. Wittstock, "Spatiotemporal changes of the solid electrolyte interphase in lithium-ion batteries detected by scanning electrochemical microscopy." *Angew. Chem. Int. Ed.*, **53**, 10531 (2014).
25. M. S. Hossain, L. I. Stephens, M. Hatami, M. Ghavidel, D. Chhin, J. I. Dawkins, L. Savignac, J. Mauzeroll, and S. B. Schougaard, "Effective mass transport properties in lithium battery electrodes." *Materials*, **3**, 440 (2019).
26. L. Zielke, T. Hutzenlaub, D. R. Wheeler, I. Manke, T. Arlt, N. Paust, R. Zengerle, and S. Thiele, "A combination of x-ray tomography and carbon binder modeling: Reconstructing the three phases of licoo2 Li-ion battery cathodes." *Adv. Energy Mater.*, **4**, 1301617 (2014).
27. E. Martin and V. Wood, "Tool for tortuosity estimation in lithium ion battery porous electrodes." *J. Electrochem. Soc.*, **162**, A3064 (2014).
28. Y.-c. K. Chen-Wiegar, R. DeMike, C. Erdonmez, K. Thornton, S. A. Barnett, and J. Wang, "Tortuosity characterization of 3D microstructure at nano-scale for energy storage and conversion materials." *Journal of Power Sources*, **249**, 349 (2014).
29. D. Kehrwald, P. R. Shearing, N. P. Brandon, P. K. Sinha, and S. J. Harris, "Local tortuosity inhomogeneities in a lithium battery composite electrode." *J. Electrochem. Soc.*, **158**, A1393 (2011).
30. S. Müller, J. Eller, M. Ebner, C. Burns, J. Dahn, and V. Wood, "Quantifying inhomogeneity of lithium ion battery electrodes and its influence on electrochemical performance." *J. Electrochem. Soc.*, **165**, A339 (2018).
31. J. Landesfeind, J. Hattendorff, A. Ehrl, W. A. Wall, and H. A. Gasteiger, "Tortuosity determination of battery electrodes and separators by impedance spectroscopy." *J. Electrochem. Soc.*, **163**, A1373 (2016).
32. N. Ogihara, S. Kawachi, C. Okuda, Y. Itou, Y. Takeuchi, and Y. Ukyo, "Theoretical and experimental analysis of porous electrodes for lithium-ion batteries by electrochemical impedance spectroscopy using a symmetric cell." *J. Electrochem. Soc.*, **159**, A1034 (2012).
33. N. A. Zacharias, D. R. Nevers, C. Skelton, K. Knackstedt, D. E. Stephenson, and D. R. Wheeler, "Direct measurements of effective ionic transport in porous Li-ion electrodes." *J. Electrochem. Soc.*, **160**, A306 (2013).
34. M. Kroll, D. Hlushkou, S. Schlögl, A. Hölzel, B. Roling, and U. Tallarek, "Reconstruction-simulation approach verifies impedance-derived ion transport tortuosity of a graphite battery electrode." *J. Electrochem. Soc.*, **165**, A3156 (2018).
35. T. DuBeshter, P. K. Sinha, A. Sakars, G. W. Fly, and J. Jorne, "Measurement of tortuosity and porosity of porous battery electrodes." *J. Electrochem. Soc.*, **161**, A599 (2014).
36. B. Suthar, J. Landesfeind, A. Eldiven, and H. A. Gasteiger, "Method to determine the in-plane tortuosity of porous electrodes." *J. Electrochem. Soc.*, **165**, A2008 (2018).
37. S. Malifarge, B. Delobel, and C. Delacourt, "Determination of tortuosity using impedance spectra analysis of symmetric cell." *J. Electrochem. Soc.*, **164**, E3329 (2017).
38. J. Landesfeind, M. Ebner, A. Eldiven, V. Wood, and H. A. Gasteiger, "Tortuosity of battery electrodes: validation of impedance-derived values and critical comparison with 3D tomography." *J. Electrochem. Soc.*, **165**, A469 (2018).
39. M. J. Martínez, S. Shimpalee, and J. W. Van Zee, "Measurement of macmullin numbers for pemfc gas-diffusion media." *J. Electrochem. Soc.*, **156**, B80 (2008).
40. K. K. Patel, J. M. Paulsen, and J. Desilvestro, "Numerical simulation of porous networks in relation to battery electrodes and separators." *Journal of power sources*, **122**, 144 (2003).
41. J. E. Vogel, E. E. Hunter, D. R. Wheeler, and B. A. Mazzeo, "Micro-flexible-surface probe for determining spatially heterogeneous electronic conductivity of lithium-ion battery electrode films." *J. Electrochem. Soc.*, **168**, 100504 (2021).
42. M. Ebner, D. Chung, R. E. García, and V. Wood, "Tortuosity anisotropy in lithium-ion battery electrodes." *Adv. Energy Mater.*, **4**, 1301278 (2014).