

Supporting Information for

***In operando* Visualization of Electrolyte Stratification Dynamics in Lead-acid Battery using phase-contrast X-ray Imaging**

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SI-1. Cell assembly and experimental conditions

The model LAB cell designed for phase-contrast X-ray phase imaging consisted of a rectangle case of glass, which can insert electrodes and an electrolyte inside. Thin glass was used in this study with respect to (i) X-ray penetration, (ii) rigidity (no deformation), and (iii) corrosion durability with the sulfuric acid electrolyte. The size of PbO₂ positive electrode is 29 mm (height) x 7 mm (width) x 3.4 mm (thickness), and that of Pb negative electrode is 29 mm x 7 mm x 1.8 mm, respectively. The assumed capacity calculated from the electrode size was approx. 130 mAh. The initial concentration of 37 wt% dilute sulfuric acid aqueous solution (specific gravity was 1.29 g/cm³) was used as the electrolytes. Photographs of the cell and pair of electrodes are shown in Fig. S1a. Schematic Top view drawing of the cell is shown in Fig. S1b. Photograph of electrodes and electrolyte region of the cell is shown in Fig. S1c. Figure S1d is typical X-ray interferometer image of electrolyte inside red dashed rectangle of Fig. S1c.

Phase-contrast X-ray imaging measurements were carried out using a 17.8 keV X-ray emitted from a vertical wiggler at the BL14C of Photon Factory (Tsukuba, Japan). The measurements were examined at room temperature. X-ray interferometer images were detected using a lens-coupled scintillator with a CCD camera (VHR, 12.5 $\mu\text{m}/\text{pixel}$). The phase image was obtained using the third step fringe scanning method. As the exposure time to obtain an interference image was 5 s, one phase-shift image could be captured every 15 s. The galvanostatic charge/discharge of the cells were carried out using a Biologic VSP by setting the lower and upper potentials as 1.75 and 3.0 V. Before *in operando* phase-contrast X-ray imaging measurement, the electrodes were pre-adjusted to the desired SOC by the low-rate (C/5 rate) charging and discharging in a beaker cell. From this offline experiment, we decided the 1C-rate current as 100 mA.

SI-2. Quantification of phase-contrast X-ray imaging

Based on Fresnel's equations, the complex index of refraction n in the hard X-ray region is given by

$$n = 1 - \delta + i\beta \quad (\text{S1})$$

where δ is refractive index decrement and β is imaginary part of refractive index.¹ The values of δ and β are proportional to the density of the medium, and δ is used as the imaging contrast for X-ray phase imaging.

From the consideration of an anomalous dispersion effect, δ is given by

$$\delta = \frac{r_e}{2\pi} \lambda^2 \sum_i n_i (Z_i + f_i') \quad (\text{S2})$$

where r_e is the classical electron radius, λ is the wavelength of X-ray, n_i is the number of atoms per unit volume, Z_i is the atomic number of each atom contained in the medium, and f_i' is the real parts of the atomic anomalous scattering factor. The f_i' values for the 17.8 keV X-ray of the atoms contained in the electrolytes are shown in Table S1.² As the f_i' values are negligibly small, it is disregarded in this study. Furthermore, n_i is given by

$$n_i = \frac{N_A \rho x_i}{\sum_i x_i M_i} \quad (\text{S3})$$

where N_A is the Avogadro constant, ρ is the electron density, x_i is the ratio of i -th element, and M_i is the molar mass of i -th element. Assuming only main electrochemical reactions exist and all the side reactions are neglected in the system, i can be considered as sulfuric acid ion (SO_4^{2-}).

The phase-shift ϕ caused by passing through the sample having a thickness of L is given by

$$\phi = \frac{2\pi L}{\lambda} \delta \quad (\text{S4})$$

Herein, we consider only change in the nominal sulfuric acid concentration (ΔC) caused by charging/discharging from the initial state, and we assume that the change in the electrolyte density ($\Delta\rho$) is proportional to ΔC at constant volume. From this assumption, we can obtain the correlation between the phase-shift change ($\Delta\phi$) and $\Delta\rho$ caused by charging/discharging from the initial state as follows,

$$\Delta\phi = L r_e \lambda N_A \frac{Z}{M} \Delta\rho \quad (\text{S5})$$

During discharge, the overall electrochemical reactions of LAB during the discharging can be described by the equation:



All quantities in Equation S5 can be strictly determined as constants, that is, $L = 0.009$ m, $r_e = 2.818 \times 10^{-15}$ m, $\lambda = 6.97 \times 10^{-11}$ m, $N_A = 6.02 \times 10^{23}$ /mol, $Z/M = 0.5$ mol/g. As a result, we can obtain the quantitative correlation between $\Delta\phi$ and $\Delta\rho$ during battery operation can be obtained as follows

$$\Delta\rho = 0.0019 \Delta\phi \quad (\text{S7})$$

SI. References

(1) Saisho, H.; Gohshi, Y. *Applications of synchrotron radiation to materials analysis*, Elsevier Science B. V., Amsterdam, **1996**.

(2) Henke, B. L.; Gullikson, E. M.; Davis, J. C. *X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at $E = 50\text{-}30,000$ eV, $Z = 1\text{-}92$* . *At. Data nucl. Data Tables* **1993**, *54*, 181.

