

Quantitative Visualization of Salt Concentration Distributions in Lithium-Ion Battery Electrolytes by *in operando* X-ray Phase Imaging

Daiko Takamatsu^a, Akio Yoneyama^a, Yusuke Asari^a, Tatsumi Hirano^a
^a *Research & Development Group, Hitachi, Ltd., Hitachi-shi, Ibaraki, Japan*

E-mail: daiko.takamatsu.hu@hitachi.com

A fundamental understanding of concentrations of salts in the electrolytes of lithium-ion batteries (LIBs) during battery operation is important for optimal operation and design of LIBs. However, there are few techniques that can be used to quantitatively characterize salt concentration distributions in the electrolytes during the battery operation. We have reported that *in operando* phase-contrast X-ray imaging technique can quantitatively visualize the salt concentration distributions that arise in electrolytes during battery operation [1-3].

Figure 1 shows (a) schematic view of the cell connected to galvanostat (GS), (b) constant-current charge profile, and (c) corresponding extracted phase-shift images of electrolyte. By using an original spectro-electrochemical cell similar to actual LIBs and a fine imaging system using synchrotron radiation, we obtained the continuous phase-shift images of the electrolyte region between the LiFePO₄ composite electrode (working electrode, WE) and the Li-metal (counter electrode, CE) during battery operation. When constant-current charge began, the phase-shift change (Δdp) in the vicinity of the WE increased while that near the CE decreased. To evaluate the salt distribution during the charging from the phase maps, we conducted a quantitative evaluation of the phase-shift changes [3]. As a result, we obtained the salt diffusivities in electrolytes with different initial salt-concentrations from the quantitative evaluation of the concentration distributions at steady-states [3]. Because of no restriction on samples, and high temporal (a few seconds) and spatial (a few μm) resolutions, phase-contrast X-ray imaging will become a versatile tool for evaluating electrolytes, both aqueous and non-aqueous, of many electrochemical systems, which will further our understanding of the dynamic behavior of electrolytes in actual applications.

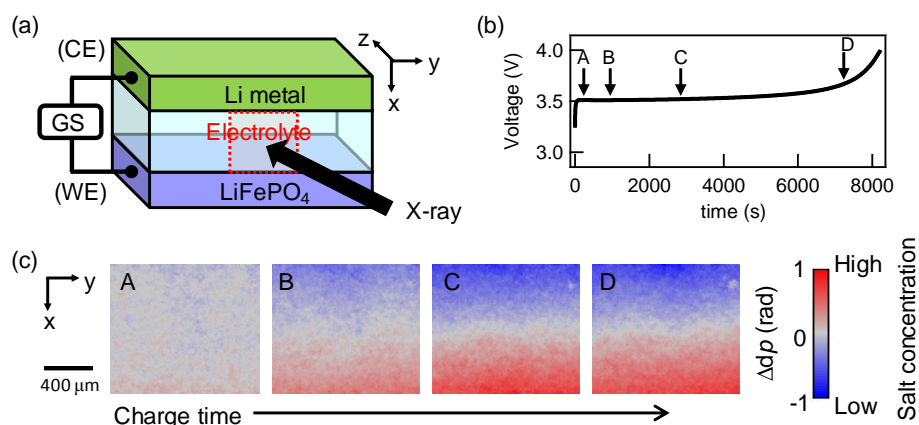


Figure 1. (a) Schematic view of spectro-electrochemical cell. (b) constant-current (0.06 mA) charge profile, and (c) corresponding extracted phase-shift change (Δdp) maps of electrolyte. Since the phase shifts are estimated as changes from the first image of $t = 0$ s (without an applied current), the Δdp reflects the change in electrolyte density caused by charging from the initial state.

References:

- [1] D.Takamatsu, A. Yoneyama, H. Hirano, The 55th Battery symposium in Japan, 3D25 (2014) .
- [2] D.Takamatsu, H. Hirano, A. Yoneyama, Y. Asari, The 56th Battery symposium in Japan, 2E25 (2015) .
- [3] D.Takamatsu, A. Yoneyama, Y. Asari, H. Hirano, *J. Am. Chem. Soc.*, accepted, DOI: 10.1021/jacs.7b13357.