

Dynamic changes in charge-transfer resistance at Li metal/Li₇La₃Zr₂O₁₂ interfaces during electrochemical Li dissolution/deposition cycles

Shoichi Matsuda^a, Hiroyuki Koshikawa^b, Yoshimi Kubo^a, Kohei Uosaki^a, Shuji Nakanishi^c

^a *Global Research Center for Environment and Energy Based on Nanomaterials Science, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

^b *Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

^c *Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*

E-mail: MATSUDA.Shoichi@nims.go.jp

Lithium (Li) metal is an attractive material for the use as the negative electrode of next-generation batteries such as Li-air and Li-sulfur batteries due to its high theoretical capacity (3860 mAh g⁻¹) and the lowest electrochemical potential (-3.040 V vs. SHE). The use of a solid electrolyte is a potential solution to these issues inherent in Li metal. Garnet-type cubic Li₇La₃Zr₂O₁₂ (LLZ) is promising as a solid electrolyte due to various advantages, including high Li-ion conductivity, high chemical stability against Li metal and high stiffness¹. However, it is known that the resistance of the Li/LLZ interface (R_{int}) is high, which interferes with the operation of a LLZ-based solid-state battery at a practical rate². To date, several attempts have been made to reduce R_{int} ; application of high external pressure and temperature, tuning the chemical composition of LLZ, modification of the surface morphology of LLZ by optimization of the particle and grain sizes, and the insertion of a lithiophilic layer between Li and LLZ. Although these studies have provided potential strategies to reduce R_{int} toward the successful operation of all-solid-state batteries, there is still limited information regarding how R_{int} dynamically changes during repetitive Li deposition/dissolution cycles.

To address this issue, AC impedance spectroscopy with a three-electrode setup, in which the interface between a working electrode and electrolyte can be examined independently from the other interface between a counter electrode and the electrolyte, is necessary. In the present work, we attempted to individually trace the dynamic change in R_{int} at a Li/LLZ interface during Li deposition and dissolution reactions through the use of the three-electrode AC impedance technique³. As a result, we clarified that the trace the dynamic changes in the charge transfer resistance at the Li/LLZ interface during Li dissolution and deposition. R_{int} increased and decreased during Li dissolution and deposition, respectively, and the increase during dissolution was not completely offset during the subsequent deposition process. Importantly, R_{int} was almost constant when Li deposition proceeded without prior Li dissolution, which suggests that the formation of voids at the Li/LLZ interface during Li dissolution is a critical factor that influences R_{int} . Based on the results obtained through the present work, we strongly encourage the development of a strategy to prevent the formation of voids at the Li/LLZ interface, particularly during Li dissolution, toward the real application of a Li metal anode in all-solid-state secondary batteries.

References:

- [1] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.*, 46 (2007) 7778–7781.
- [2] S. Ramakumar, C. Deviannapoorani, L. Dhivya, L.S. Shankar, R. Murugan, *Prog. Mater. Sci.*, 88 (2017) 325–411.
- [3] H. Koshikawa, S. Matsuda, K. Kamiya, M. Miyayama, Y. Kubo, K. Uosaki, K. Hashimoto, S. Nakanishi, *J. Power Sources*, 376 (2018) 147–151.