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Short communication

Dynamic changes in charge-transfer resistance at Li metal/$Li_7La_3Zr_2O_{12}$ interfaces during electrochemical Li dissolution/deposition cycles

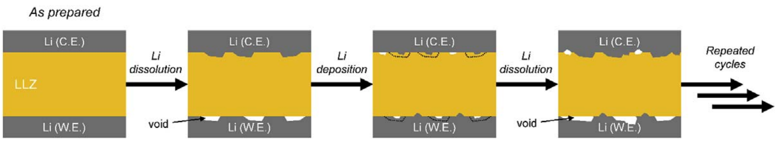
Hiroyuki Koshikawa[a], Shoichi Matsuda[b], Kazuhide Kamiya[c,d], Masaru Miyayama[a], Yoshimi Kubo[b], Kohei Uosaki[b], Kazuhito Hashimoto[b], Shuji Nakanishi[c,d,e,*]

[a] *Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Global Research Center for Environment and Energy Based on Nanomaterials Science, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[c] *Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*
[d] *Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*
[e] *Panasonic Science Research Alliance Laboratories, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

HIGHLIGHTS

- Dynamic changes in R_{int} during Li dissolution/deposition cycles were investigated.
- R_{int} respectively increased and decreased during Li dissolution and deposition.
- The change in R_{int} during dissolution was larger than that during deposition.
- R_{int} was almost constant when Li deposition proceeded without prior Li dissolution.
- The voids formation at the interface during dissolution caused the increase in R_{int}.

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamic changes in the charge-transfer resistance at a Li/$Li_7La_3Zr_2O_{12}$ (LLZ) interface during lithium (Li) dissolution/deposition cycles are investigated with an alternative current (AC) impedance technique in a three-electrode system. The resistance respectively increases and decreases during electrodissolution and electrodeposition of Li. The resistance does not return to the initial value after one cycle of Li dissolution and deposition, which indicates that the change in resistance during dissolution is larger than that during deposition. Furthermore, the resistance is almost constant when Li deposition proceeds without prior Li dissolution. The respective increase and decrease in the interfacial resistance during Li dissolution and deposition is most likely due to the formation and disappearance of voids at the Li/LLZ interface, and the voids formation during Li dissolution is suggested to be a critical factor that influences the interfacial resistance.

1. Introduction

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) [1–10].

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[*] Corresponding author. Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.
E-mail address: nakanishi@chem.es.osaka-u.ac.jp (S. Nakanishi).

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Nevertheless, the practical use of Li metal as a negative electrode for secondary batteries has not yet been realized due to issues such as the consumption of Li metal by side reactions with electrolyte and the short-circuit by the growth of Li dendrites [11–14]. The use of a solid electrolyte is a potential solution to these issues inherent in Li metal. Garnet-type cubic $Li_7La_3Zr_2O_{12}$ (LLZ) is promising as a solid electrolyte due to various advantages, including high Li-ion conductivity, high chemical stability against Li metal and high stiffness [11–19]. 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 rate [13,14,16,18].

Previous studies have revealed that various factors determine R_{int}, including the segregation of impurities (e.g. Li_2CO_3) at the interface [20–22], poor physical contact between Li and LLZ [18,23], and slow interfacial charge transfer [20,24–26]. To date, several attempts have been made to reduce R_{int}; application of high external pressure [26,27] and temperature [28,29], tuning the chemical composition of LLZ [24], modification of the surface morphology of LLZ by optimization of the particle and grain sizes [21–23,25,30], and the insertion of a lithiophilic layer between Li and LLZ [31–37]. 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.

Alternating current (AC) impedance spectroscopy is a non-destructive method used to examine the time transient of the resistance in an electrolyte and at an electrode/electrolyte interface. The AC impedance technique has been recently applied to study Li/LLZ interfaces *in situ* during repetitive Li deposition/dissolution cycles [23,26,28,37]. In these reports, the increase in R_{int} measured using symmetrical Li/LLZ/Li cells was interpreted to be derived from the deterioration of the physical contact between Li and LLZ due to void formation during Li dissolution on one electrode. However, for the two-electrode system, the information from two Li/LLZ interfaces were indivisibly included in the impedance spectra. Therefore, the rise in R_{int} thus measured cannot, in principle, be assigned to either Li deposition or dissolution, despite the significant importance of knowing which reaction should be controlled more precisely to realize high-rate and long-life batteries. 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 technique.

2. Experimental

2.1. Preparation of LLZ powder and pellets

LLZ powder was prepared by the conventional solid-state method [38,39]. Lithium hydroxide monohydrate (Kanto Chemical Co., Inc., 98.0%), Lanthanum hydroxide (Kojundo Chemical Laboratory Co., Ltd., 99.99%), Zirconium oxide (Tosoh Co.) were mixed in a molar ratio of 7.7:3:2 with 10% excess Li source to compensate for the loss of Li during calcination. The mixture was ball-milled in hexane at 400 rpm intermittently for 2 h with zirconia balls (5 mm diameter) in a planetary ball-mill (Pulverisette 6, Fritsch). The mixed powder was calcined in an alumina crucible at 900 °C for 15 h in air, and then the calcined powder was mixed with γ-aluminum oxide (Kojundo Chemical Laboratory Co., Ltd., 99.99%) according to the nominal formula of $Al_{0.25}Li_{6.25}La_3Zr_2O_{12}$ by planetary ball-milling in the same way. The obtained powder was sieved to below 710 μm and pressed into a pellet of 15 mm diameter under a pressure of 20 MPa for 5 min. The pellets were covered by protective mother powder with the same composition in an alumina crucible, and sintered at 900 °C for 3 h and then at 1200 °C for 24 h in air. X-ray diffraction (XRD) measurement of the powder sample obtained by fracturing the pellet after sintering confirmed that LLZ with a cubic structure was successfully prepared (Fig. S1(a)). After sintering, the pellets were polished to a thickness of 800 μm in air, and dried at 110 °C overnight under vacuum to remove the residual water. The surface was then finally polished with emery paper (#4000) in an argon-filled glove box with a water content of less than 1 ppm to ensure the removal of the resistive Li_2CO_3 layer formed on the surface [20]. Although some micropores due to Li evaporation during sintering were observed using field-emission scanning electron microscopy (SEM), the grains with the size of several hundreds of μm were well grown with intimate connections between them (Fig. S1(b)). The relative density of the LLZ pellet was calculated to be 94% by dividing the bulk density by the theoretical density (5.1 $g\ cm^{-3}$), which was in the range of the reported values (90–99%). These results indicated that a well-sintered and dense LLZ pellet was obtained. The Li-ion conductivity of the LLZ pellet was measured following a well-established protocol [38], and then calculated to be 1.2×10^{-4} $S\ cm^{-1}$ (Fig. S1(c)), which is in the range of previously reported values [15,23–25,30,38].

2.2. Characterization of LLZ

XRD (D8 ADVANCE, Bruker) patterns were recorded with a step size of 0.015° and a collection time of 1 s at 40 kV and 40 mA over the 2θ angular range between 10° and 70°. SEM (JSM-7800F, JEOL) was used to observe the cross-section of a LLZ pellet. The sample was transferred from the glove box to the SEM instrument in a sealed vessel filled with argon gas. Measurements were conducted at an acceleration voltage of 5 kV under an ambient pressure of less than 10^{-4} Pa.

2.3. Cell assembly and electrochemical measurements

A three-electrode cell was assembled using metallic-Li foil (3 mm diameter, 400 μm thick, Honjo Metal Co., Ltd.) as both working electrode (W.E.) and counter electrode (C.E.), and a metallic-Li ring (outer diameter = 10 mm, inner diameter = 8 mm, Honjo Metal Co., Ltd.) was used as a reference electrode (R.E.), as shown in Fig. S2. The surface of the metallic-Li electrodes was polished with emery paper (#4000) to remove the passivation layer formed on the surface. Assembled cells were heated at 100 °C for 4 h in air before electrochemical measurements.

Galvanostatic Li dissolution/deposition and AC impedance measurements were conducted at 25 °C using a potentio-galvanostat equipped with an impedance analyzer (VMP3, BioLogic Science Instruments). AC impedance spectra were collected with an amplitude of 15 mV in the frequency range from 1 MHz to 100 Hz. For measurement of the Li-ion conductivity, a symmetrical Au/LLZ/Au cell, in which Au was sputtered on both surfaces of the LLZ pellet as ion blocking electrodes, was also utilized.

3. Results and discussion

The dynamic changes in the charge transfer resistance at the Li/LLZ interface during Li dissolution/deposition cycles were investigated using the three-electrode AC impedance technique to individually clarify the influence of Li dissolution and deposition on the resistance. In this experiment, Li was repeatedly dissolved and deposited for 1 h at 50 $\mu A\ cm^{-2}$, and AC impedance measurement was conducted every 10 min during the cycle test. Fig. 1 shows representative Nyquist plots obtained during the test. An equivalent circuit used for fitting the plots was composed of two series of the parallel combination of resistance and constant phase element (CPE) as shown in the inset of Fig. 1. The subscript LLZ and int means the contribution from LLZ solid electrolyte and Li (W.E.)/LLZ interface, respectively. Fig. 2(a) and (b) show the time courses of the W.E. potential and R_{int}, respectively. The overpotential increased during Li dissolution, whereas it continued to