Supporting Information:

Reducing Impedance at a Li-Metal Anode/Garnet-Type Electrolyte Interface Implementing Chemically Resolvable In Layers

Marius Müller [a], Johannes Schmieg [a,b], Sebastian Dierickx [a], Jochen Joos [a], André Weber [a], Dagmar Gerthsen [b] and Ellen Ivers-Tiffée [a]

[a] *Institute for Applied Materials (IAM-ET), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany*

[b] *Laboratory for Electron Microscopy (LEM), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany*

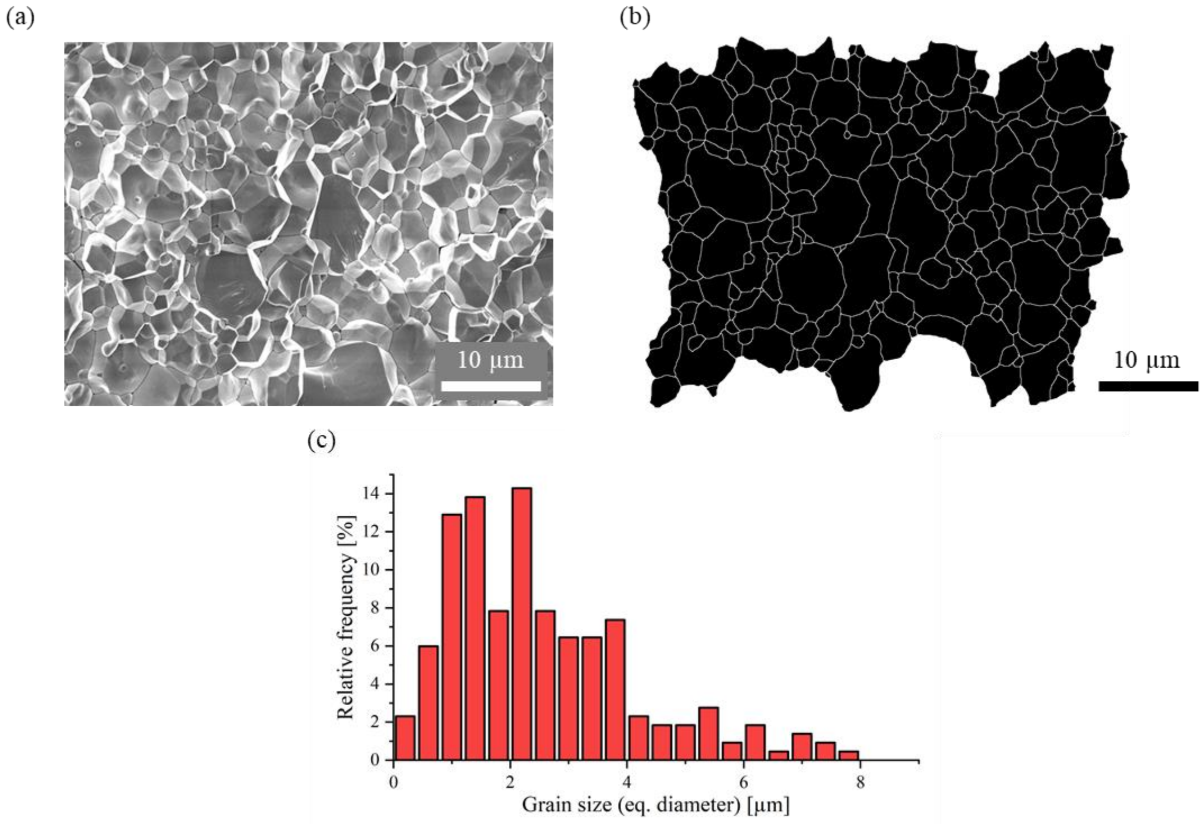


Figure S1. (a) Scanning electron microscopy (SEM) image of a fractured LLZO pellet, (b) manual segmentation of 217 grains from the SEM image in (a), (c) grain size distribution obtained from the grain areas as equivalent diameter of circular grains.

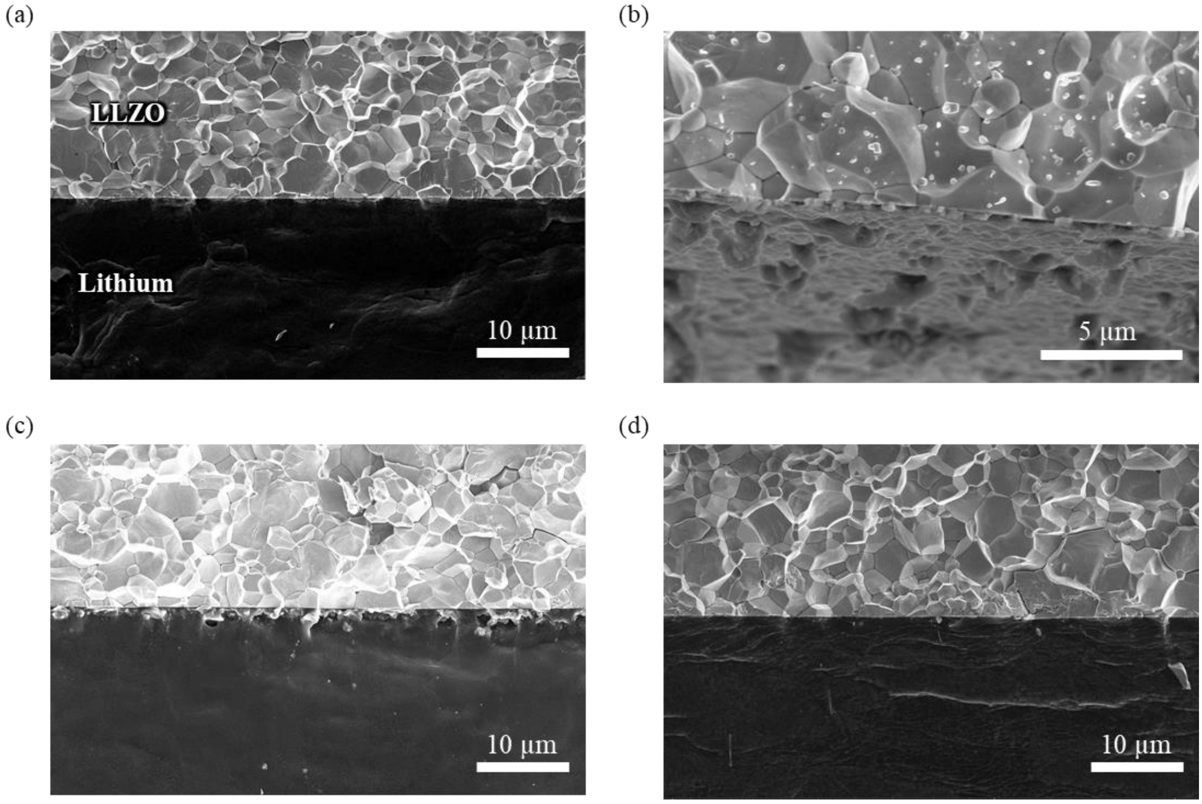


Figure S2. Comparison of as-prepared samples with different fabrication parameters: (a) contacted and (b) uncontacted Li/LLZO interface in a sample with thin In-layer (15 s sputtering time) after 2 h/220 °C annealing. The In-layer is still visible in the uncontacted region. (c) Contacted Li/LLZO interface for a thick In-layer (300 s sputtering time) after 2 h/220 °C annealing. This interface shows some small pores. (d) Li/LLZO interface with an In-layer with standard thickness (60 s sputtering time) after annealing at higher temperature (250 °C) for 2 h. No significant difference in microstructure compared to the lower annealing temperature is observed. All SEM images were taken with secondary electrons at 5 keV electron energy.

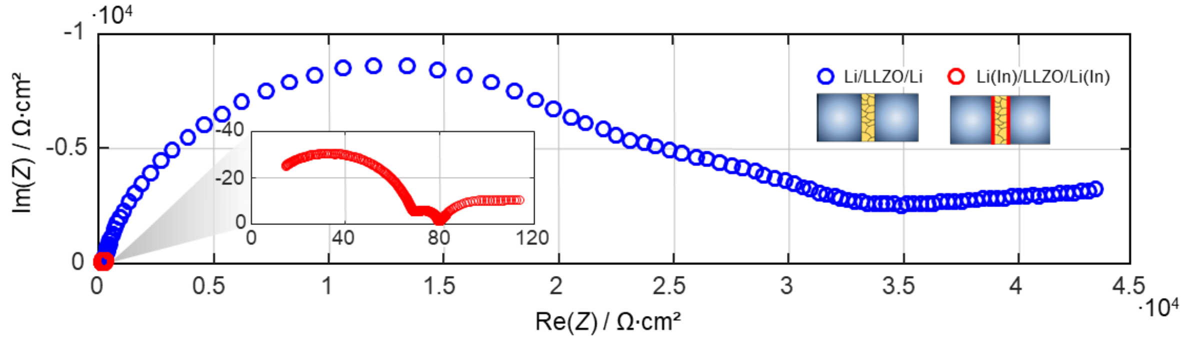
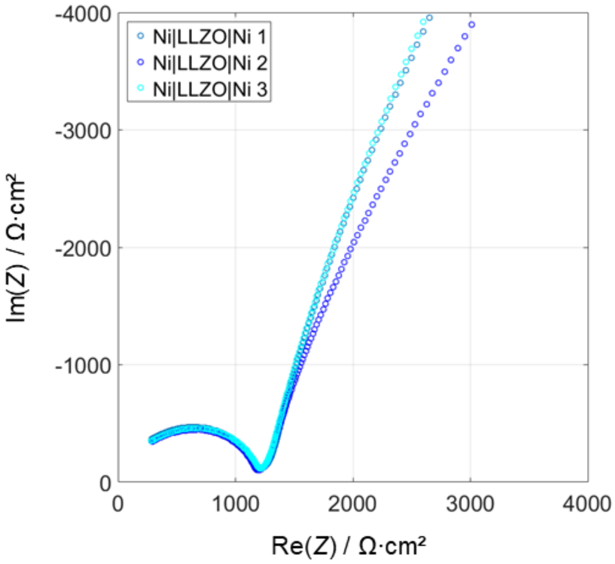


Figure S3. (a) Comparison of EIS data measured at a symmetrical Li(In)/LLZO/Li(In) (60_250_2; red circles) and a symmetrical Li/LLZO/Li cells (blue circles) without In-layer at 25 °C.

(a)



(b)

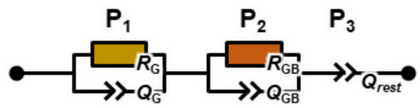


Figure S4. (a) EIS data of three symmetric Ni/LLZO/Ni cells with blocking electrodes at 25 °C measured with the HF setup (perturbation amplitude 20 mV) and (b) the corresponding equivalent circuit model consisting of two serial RQ-elements added with an CPE-element to cover the low frequency part.

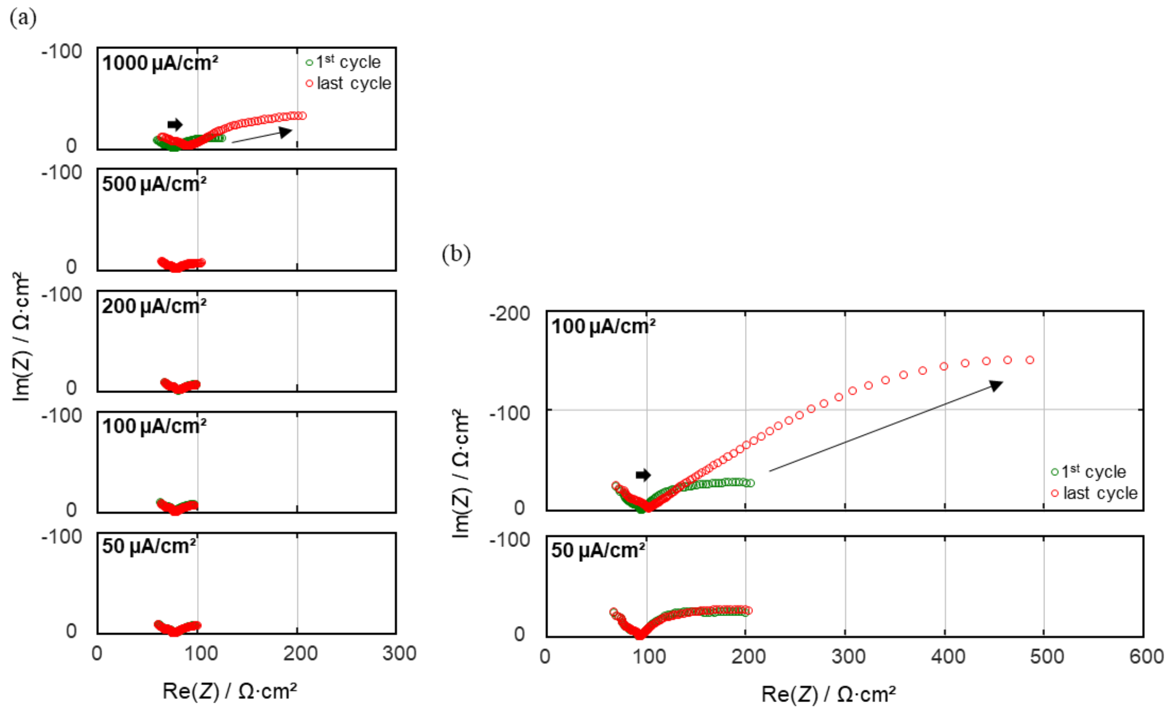


Figure S5. Temporal evolution of EIS data at 25 °C from symmetrical Li(In)/LLZO/Li(In) cells during (a) CCD test protocol I and (b) CCD test protocol II.

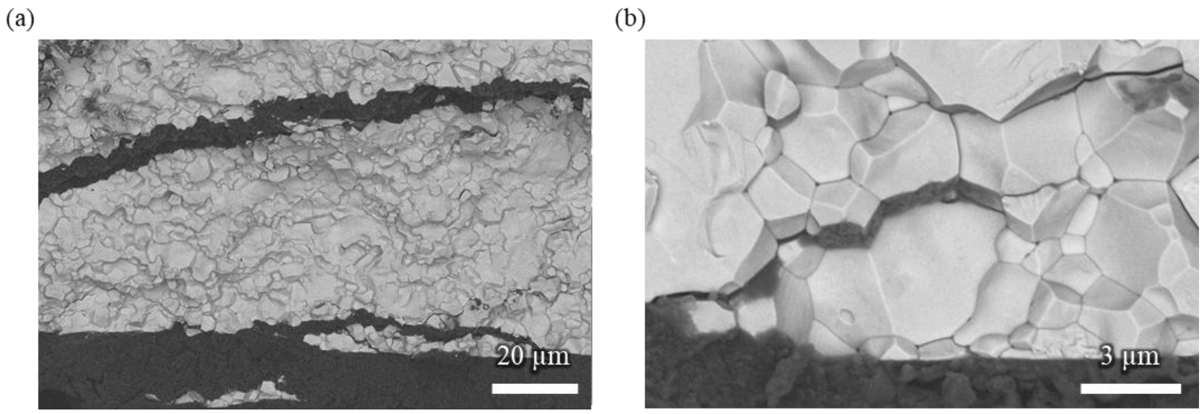


Figure S6. (a) BSE-SEM overview image of a lithium dendrite after cycling in the cell with 60 s indium sputtering time and 2 h/250 °C annealing. A maximum lithium penetration depth in the solid electrolyte of 70µm is observed. (b) Detail image of a lithium dendrite close to the Li/LLZO interface. Dendrite growth propagates along LLZO grain boundaries. The electron energy was 5 keV in both images.

Table S1: Measurement device specifications of high-frequency (HF) and low-frequency (LF) setups (ex: excitation signal).

Device	Frequency range / Hz	I_{ex} / A | U_{ex} / V	Potentiostat
Biologic VMP-300	$10 \cdot 10^{-6} - 7 \cdot 10^{6}$	$1 \cdot 10^{-9} - 1$ | $0.5 \cdot 10^{-3} - 2.5$	Yes
Keysight E4990A-120	$20 - 120 \cdot 10^{6}$	$200 \cdot 10^{-6} - 20 \cdot 10^{-3}$ | $5 \cdot 10^{-3} - 1$	No

Overview of the applied test categories

In essence, the experiments carried out are classified in three categories, which are explained below:

1. *Cell reproducibility*: All 37 Li(In)/LLZO cells with different preparation conditions are first measured at 25 °C. The acquired impedance data pass quality control and are evaluated only if three consecutive HF and LF data sets coincide without significant deviation.

2. *Temperate variation*: A temperature variation is performed on the Li(In)/LLZO cells for deconvoluting diverse physical processes and for determining the respective activation energy. EIS measurements from f_{max} = 120 MHz to f_{min} = 50 mHz start at 25 °C and, after 3 h of thermal equilibration, subsequently run through 10, 15, 20, 30, 40 and 50 °C, before a second measurement at 25 °C confirms cell stability over the entire test program. The perturbation amplitudes chosen are 20 mV (120 MHz to 20 Hz) and 2 mV (20 Hz to 50 mHz).

3. *Cycling Stability*: The galvanostatic cycling is performed on the Li(In)/LLZO cells using the *Biologic* VMP-300 multipotentiostat with a current control resolution of 0.8 pA and voltage measurement accuracy below 1 mV. Two different cycling protocols are specified in this work. The goal is to determine the critical current densities, for which the cells show stable performance in the case of (i) lithium plating only on one electrode and stripping only on the other electrode (CCD protocol I) and (ii) Li plating and stripping on the same electrode (CCD protocol II).

    a. In *CCD protocol I* a negative constant current (CC) pulse is followed immediately by a positive pulse (each applied for 30 minutes). Afterwards, the OCV was recorded for one hour and the impedance was measured from 7 MHz to 50 mHz. This loop is repeated for 35 times and then the discharge/charge current density is subsequently increased to 100, 200, 500 and 1 mA/cm² until cell failure.

    b. In case of *CCD protocol II* the current pulse length is set to 30 minutes, after which the open circuit voltage (OCV) is recorded for two hours. Thereafter, EIS measurements are performed from 7 MHz to 50 mHz for 27 times before the current density is doubled.

A detailed overview of the performed experiments, including all temperature steps and cycling currents, is given in Table S2.

Table S2: Testing methods of the assembled cells. The devices, most important parameters and measurement protocols are listed for a better overview (CCD: Critical Current Density).

Cell testing method	Devices	T / °C	f / Hz	Measurement protocol
Cell reproducibility	(E4990A +) VMP 300	25 °C	$(120)\ 7 \cdot 10^{6} - 5 \cdot 10^{-2}$	Repeated EIS cycles until stable impedance data
Temperature variation	E4990A + VMP 300	-10 - 40 °C	$1.2 \cdot 10^{8} - 5 \cdot 10^{-2}$	25 °C → 40 °C → 20 °C→ 10 °C→ 0 °C → 25 °C; 3 hours waiting time in between
CCD protocol I	VMP 300	25 °C	$7 \cdot 10^{6} - 5 \cdot 10^{-2}$	$CC_{-50\ \mu A/cm^2,\ 30\ min}$→ $CC_{+50\ \mu A/cm^2,\ 30\ min}$ → $OCV_{1\ hour}$ → EIS; 35 times; then CC steps were increased to 100, 200, 500 and 1000 µA/cm² until failure
CCD protocol II	VMP 300	25 °C	$7 \cdot 10^{6} - 5 \cdot 10^{-2}$	$CC_{+50\ \mu A/cm^2,\ 30\ min}$→ $OCV_{2\ hours}$ → EIS; 27 times; then CC step was doubled until failure