

## Supporting Information

# Solid Electrolyte Interphase Layer Formation during Lithiation of Single Crystal Silicon Electrodes with a Protective Aluminum Oxide Coating

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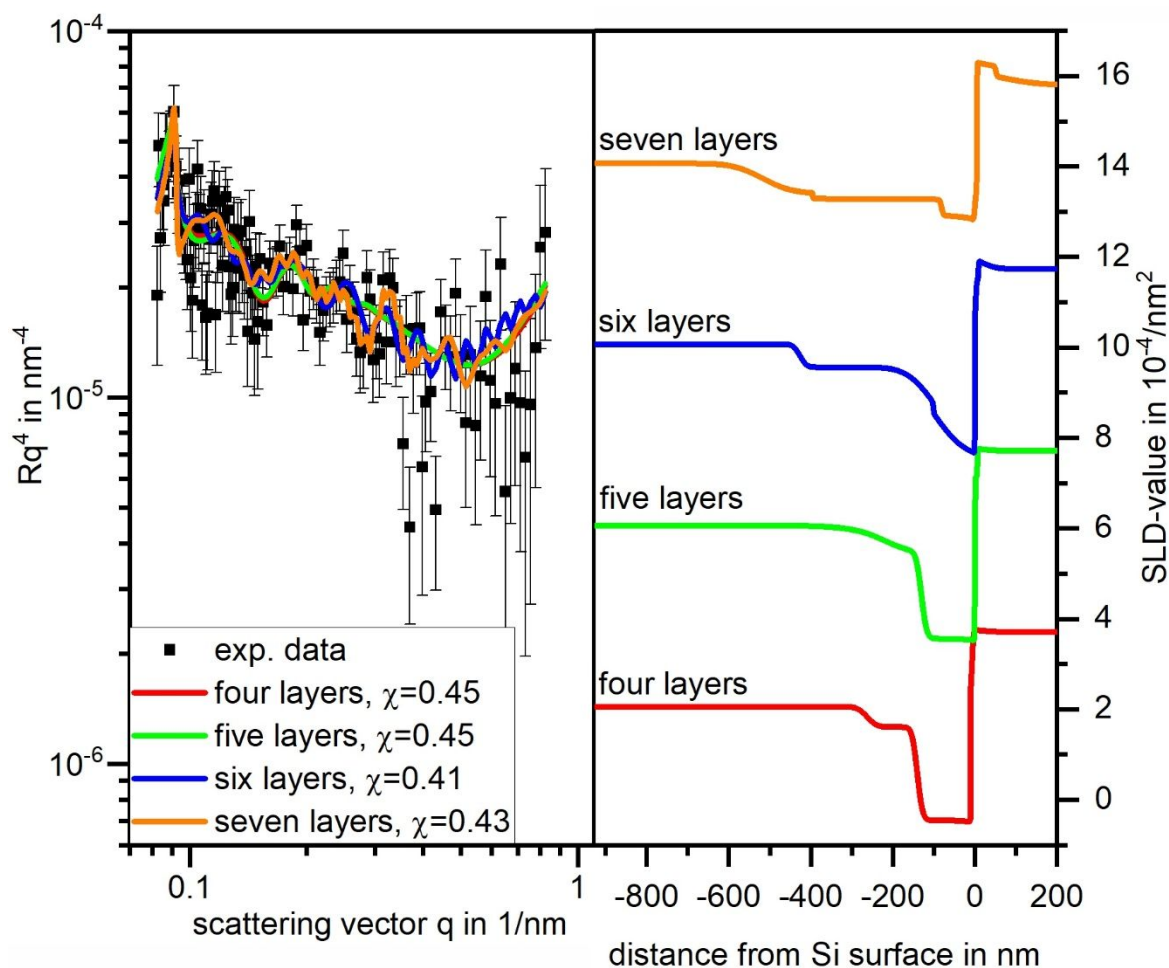


Figure S1: Optimization of the SLD-model. Four different layer-numbers were tested against an intermediate lithiated state. A 6-layer model showed the lowest residuum and was therefore chosen to analyze the data.

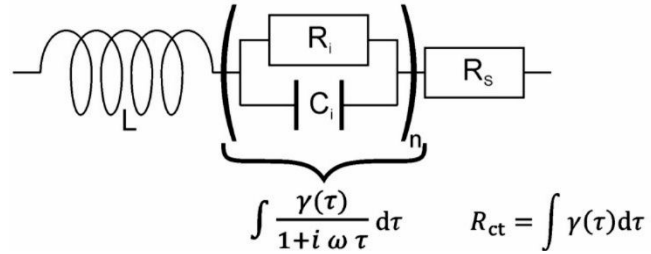


Figure S2: Equivalent circuit used for the analysis of the EIS-measurement. The distribution of relaxation times  $\gamma(\tau)$  is split into a fast ( $\tau < 1.5$  s) and a slow ( $\tau > 1.5$  s) part.

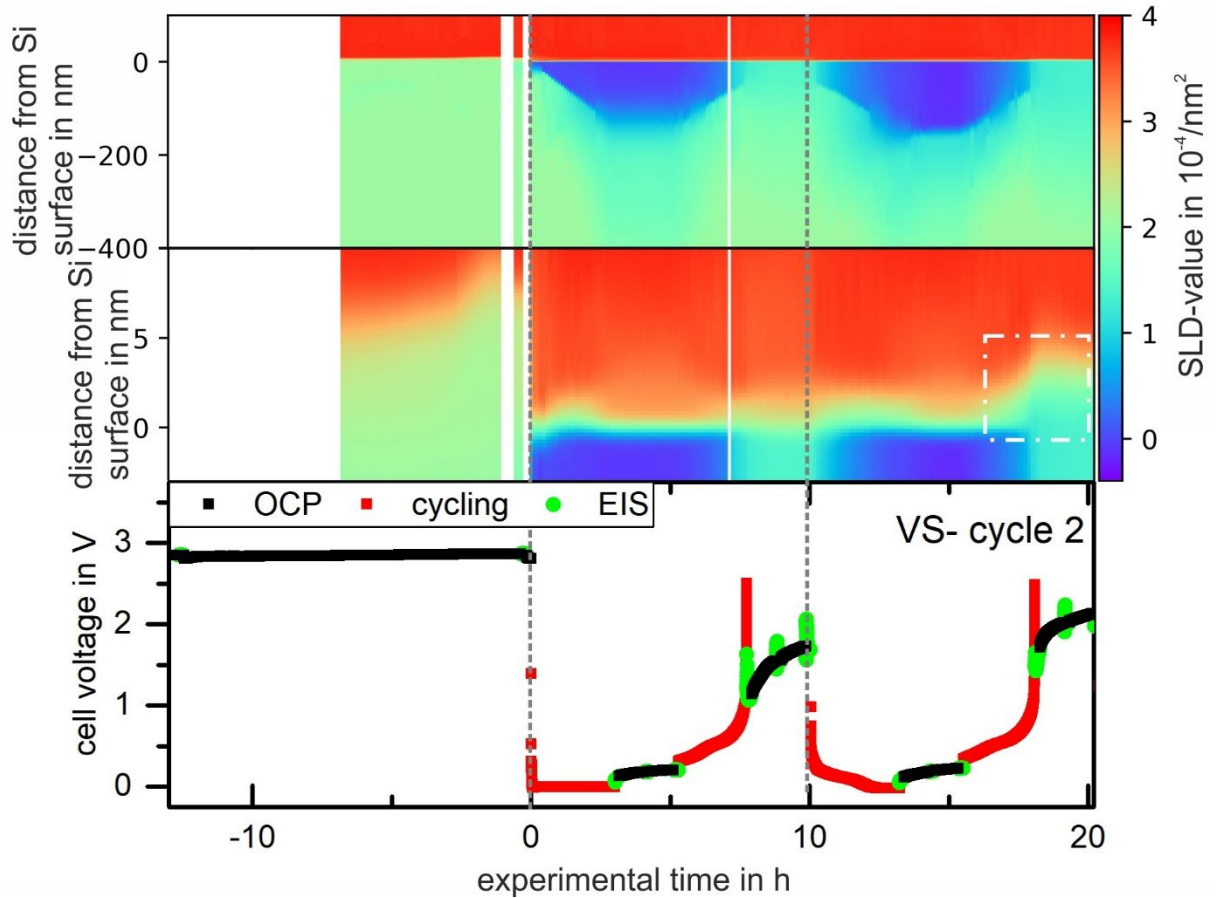


Figure S3: SLD-pattern of the virgin state up to the second cycle. On top the SLD-map of the whole depth is shown, in the middle a zoom-in to the surface. The voltage is shown at the bottom. Dashed lines indicate the beginning of a cycle. The white rectangle indicates the decomposition of the artificial SEI-layer.

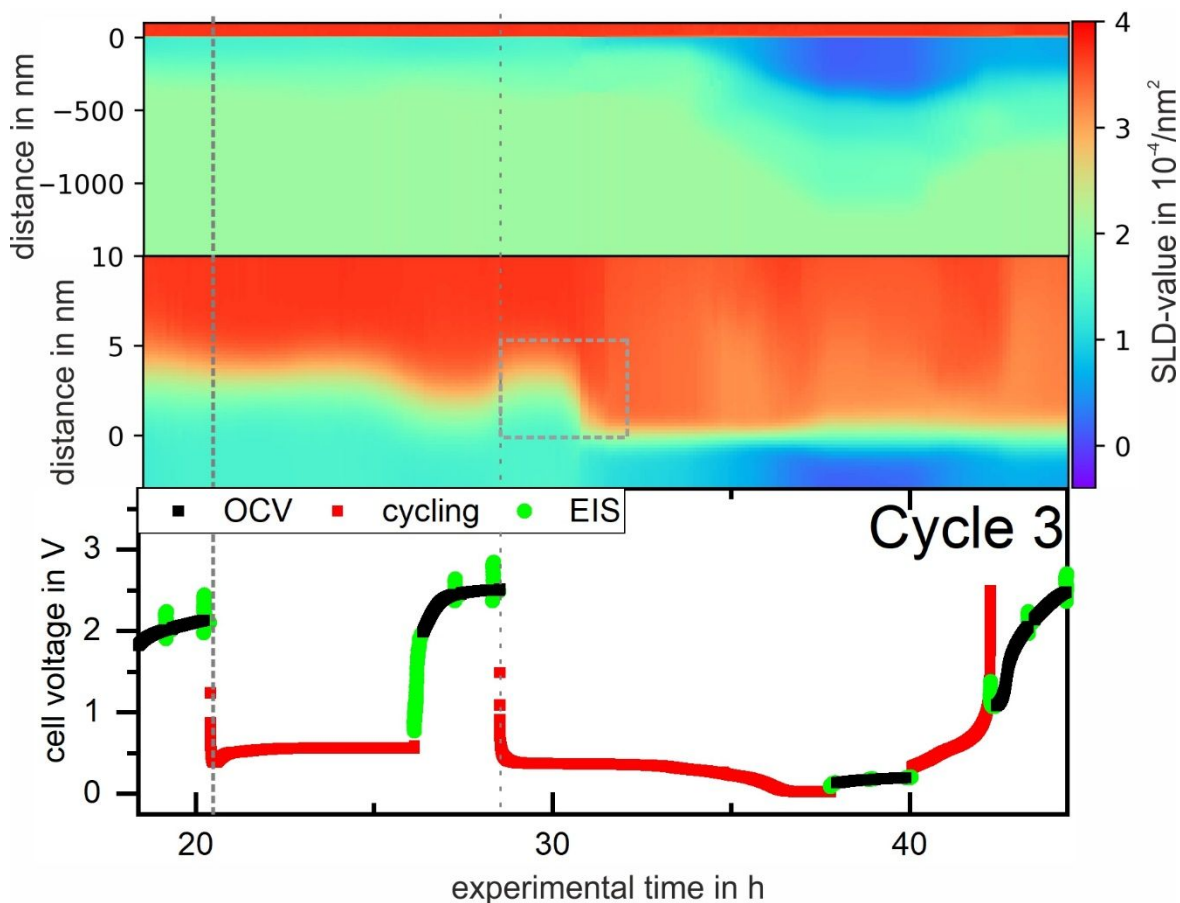


Figure S4: SLD-pattern of the third cycle. On top the SLD-map of the whole depth is shown, in the middle a zoom-in to the surface. The voltage is shown at the bottom. Dashed lines indicate the beginning of a cycle. The grey rectangle indicates the decomposition SEI-layer, which delays the lithiation process.

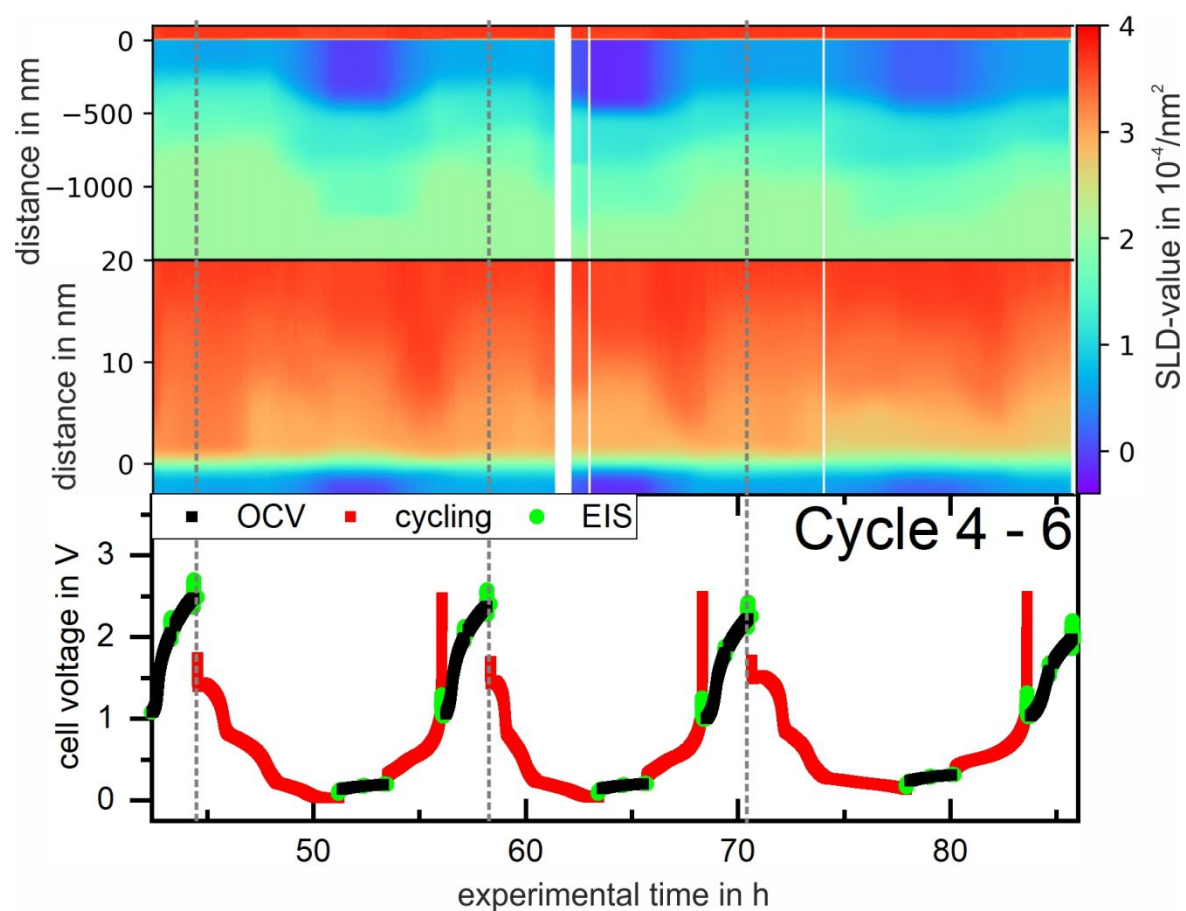


Figure S5: SLD-pattern of the fourth to sixth cycle. On top the SLD-map of the whole depth is shown, in the middle a zoom-in to the surface. The voltage is shown at the bottom. Dashed lines indicate the beginning of a cycle.

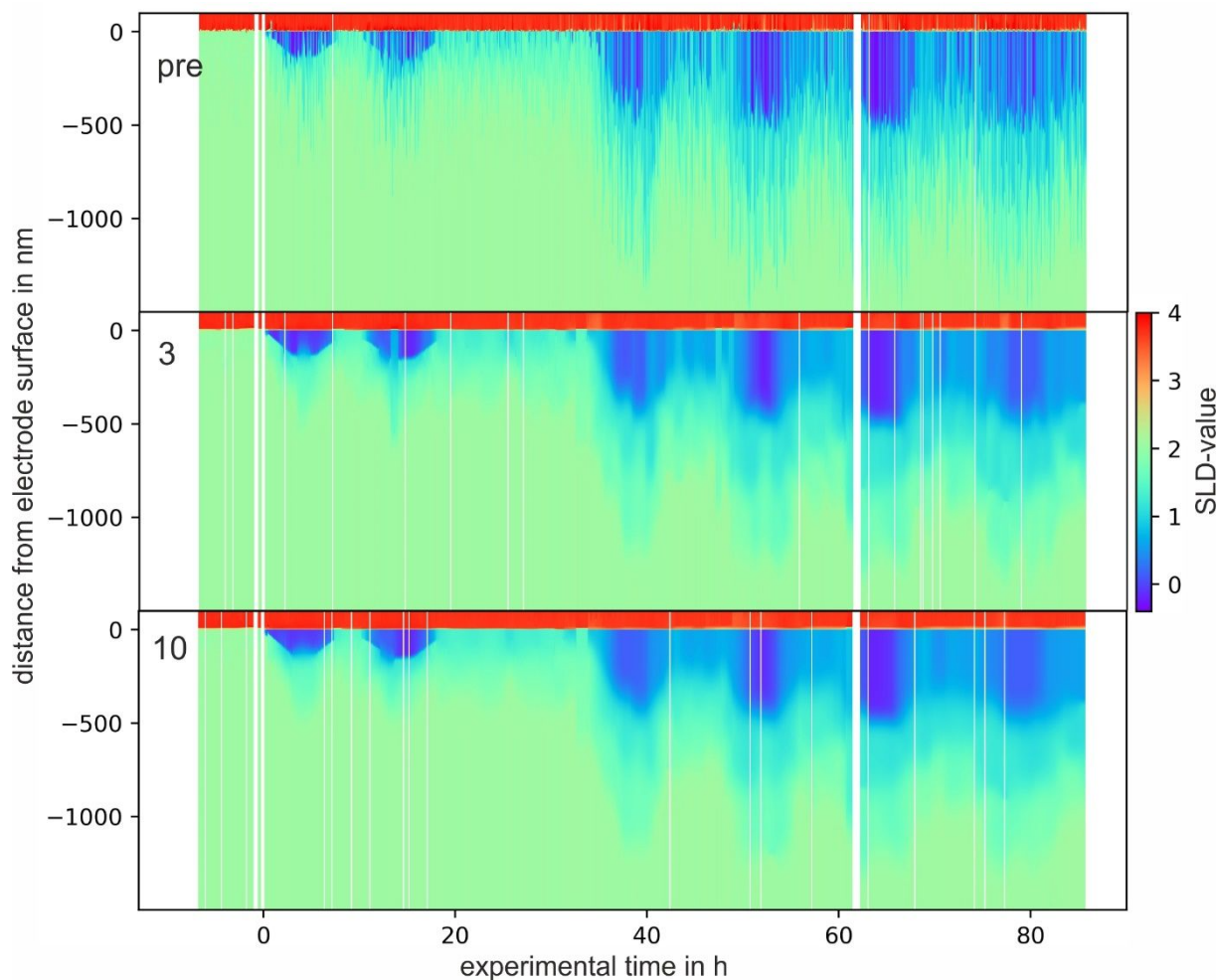
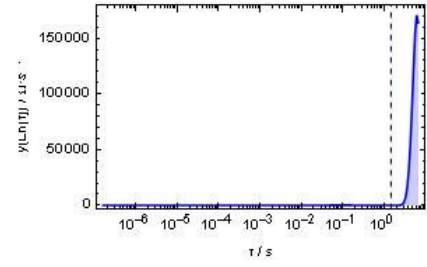
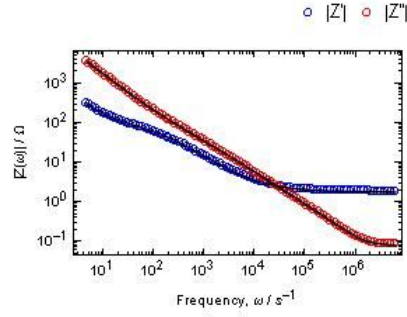


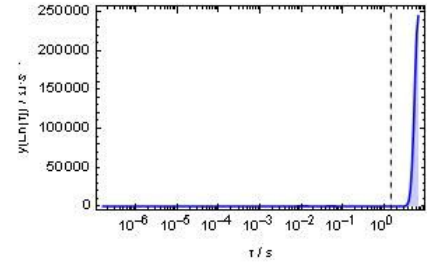
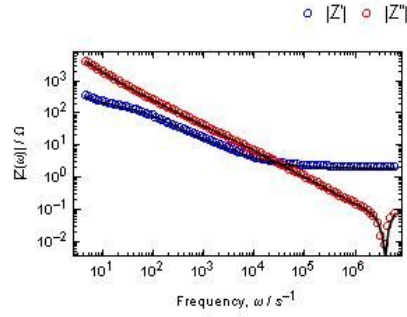
Figure S6: Evolution of the SLD-map during fit-rounds. On top, the SLD-map after the initial fitting is shown without taking neighboring profiles into account. The observed differences between the profiles are not meaningful since they result from a continuous data-acquisition (*operando*-measurement). Therefore the neighboring profiles were taken into account. The resulting SLD-map after 3 and 10 cycles is shown in the middle and at the bottom, respectively. The reflectivity- and charge-residuum do not increase significantly. The white stripes denote the absence of reflectivity data due to beam off periods.



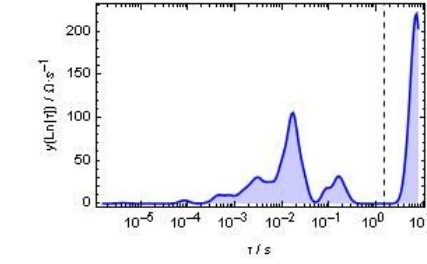
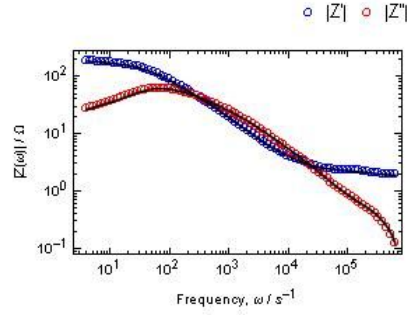
PWREISPOt-start_zhit.txt	
Exp. Time / h	-12.68
Rs / $\Omega$	1.67541
L / H	$7.02216 \times 10^{-11}$
RelError / %	0.522765
iterations	30000
Calc. Time [s]	0.9



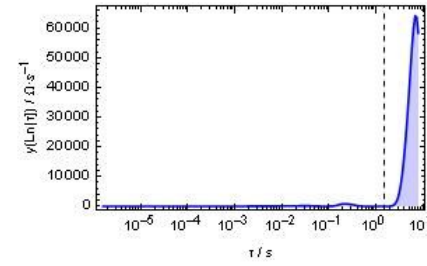
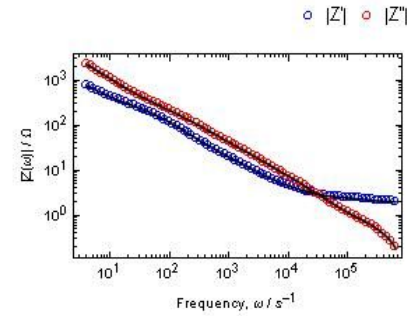
PWREISPOt-after_wetting_zhit.txt	
Exp. Time / h	-0.37
Rs / $\Omega$	1.88067
L / H	$1.98603 \times 10^{-8}$
RelError / %	1.01767
iterations	30000
Calc. Time [s]	1.2



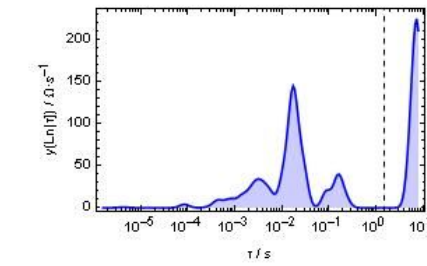
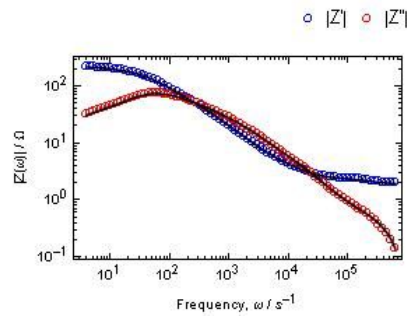
PWRHYBRIDEIS-lith-2_H1_zhit.txt	
Exp. Time / h	5.13
Rs / $\Omega$	1.82318
L / H	$2.36353 \times 10^{-7}$
RelError / %	0.55545
iterations	30000
Calc. Time [s]	0.3



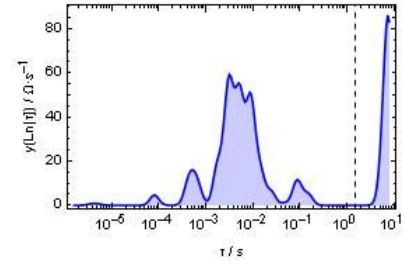
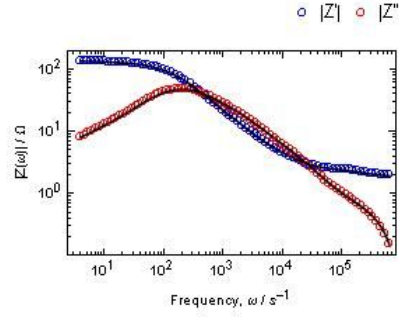
PWRHYBRIDEIS-delith-1_H1_zhit.txt	
Exp. Time / h	8.82
Rs / $\Omega$	1.91463
L / H	$2.06515 \times 10^{-7}$
RelError / %	0.554728
iterations	30000
Calc. Time [s]	0.5



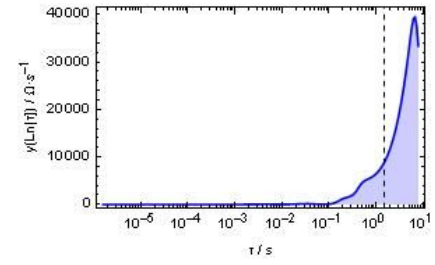
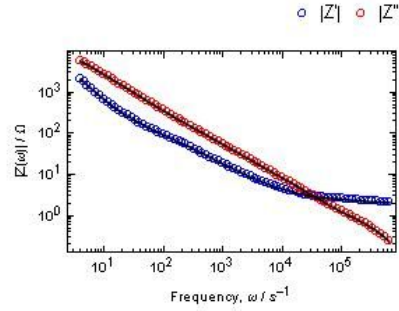
PWRHYBRIDEIS-lith-2_H2_zhit.txt	
Exp. Time / h	15.36
Rs / $\Omega$	1.85751
L / H	$2.4047 \times 10^{-7}$
RelError / %	0.573146
iterations	30000
Calc. Time [s]	0.5



PWRHYBRIDEIS-lith-1_#1 (2)_zhit.txt	
Exp. Time / h	38.83
Rs / $\Omega$	1.8345
L / H	$2.7348 \times 10^{-7}$
RelError / %	0.609807
iterations	30000
Calc. Time [s]	0.4



PWRHYBRIDEIS-delith-2_#2 (2)_zhit.txt	
Exp. Time / h	58.17
Rs / $\Omega$	2.02082
L / H	$1.2241 \times 10^{-7}$
RelError / %	0.409758
iterations	30000
Calc. Time [s]	0.4



PWRHYBRIDEIS-delith-1_#3_zhit.txt	
Exp. Time / h	69.39
Rs / $\Omega$	2.02412
L / H	$1.23793 \times 10^{-7}$
RelError / %	0.430002
iterations	30000
Calc. Time [s]	0.8

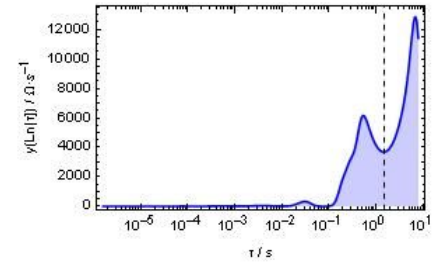
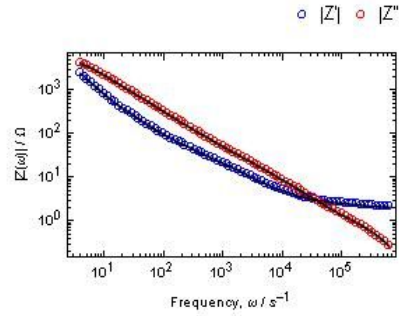


Figure S7: Selection of the EIS analysis results and the corresponding fits.