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High cyclic reversibility in Eutectic Lithium Calcium Anodes characterised by Electron Microscopy†

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1 Supplementary Figures

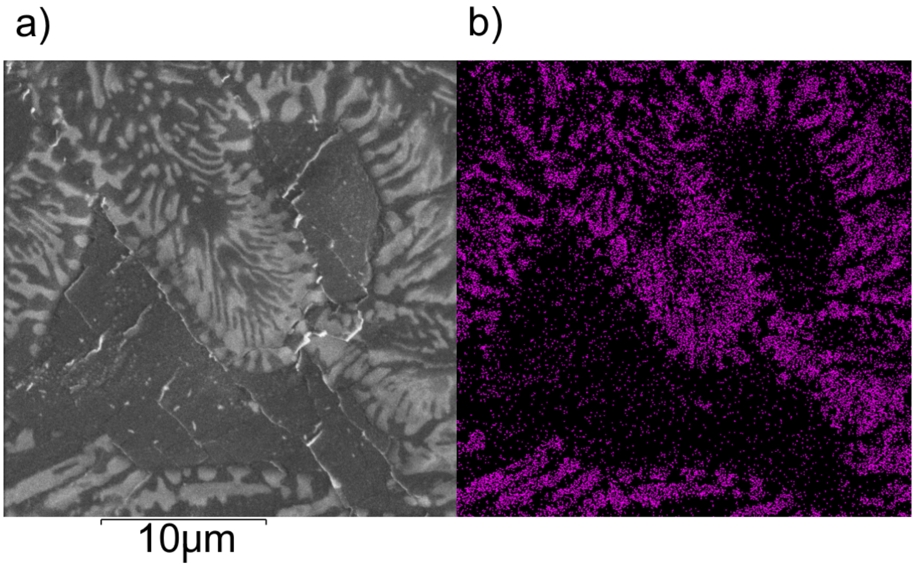

Fig. 1 a) SEM and b) EDX images of the calcium (light-SEM and purple-EDX) distribution between the phases in the LREM.

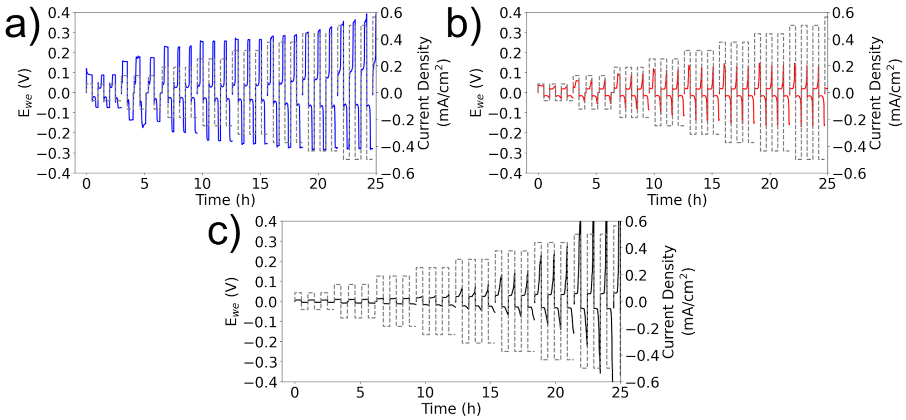

Fig. 2 Comparison of cell potential with increasing current (dashed line) focusing on the first 25 hrs of the tests. a-b) LREM symmetric cells with $LiPF_6$ and LiTFSI, respectively. c) lithium symmetric cell with LiTFSI.

1.1 Calculation of theoretical capacity.

Theoretical capacity of an anode: Electrode Mass x 58.7% x Avagadro's Number x e / Atomic mass Li x Area reference for 1.1 mA cm2 cycling is Ng cell AF or AG

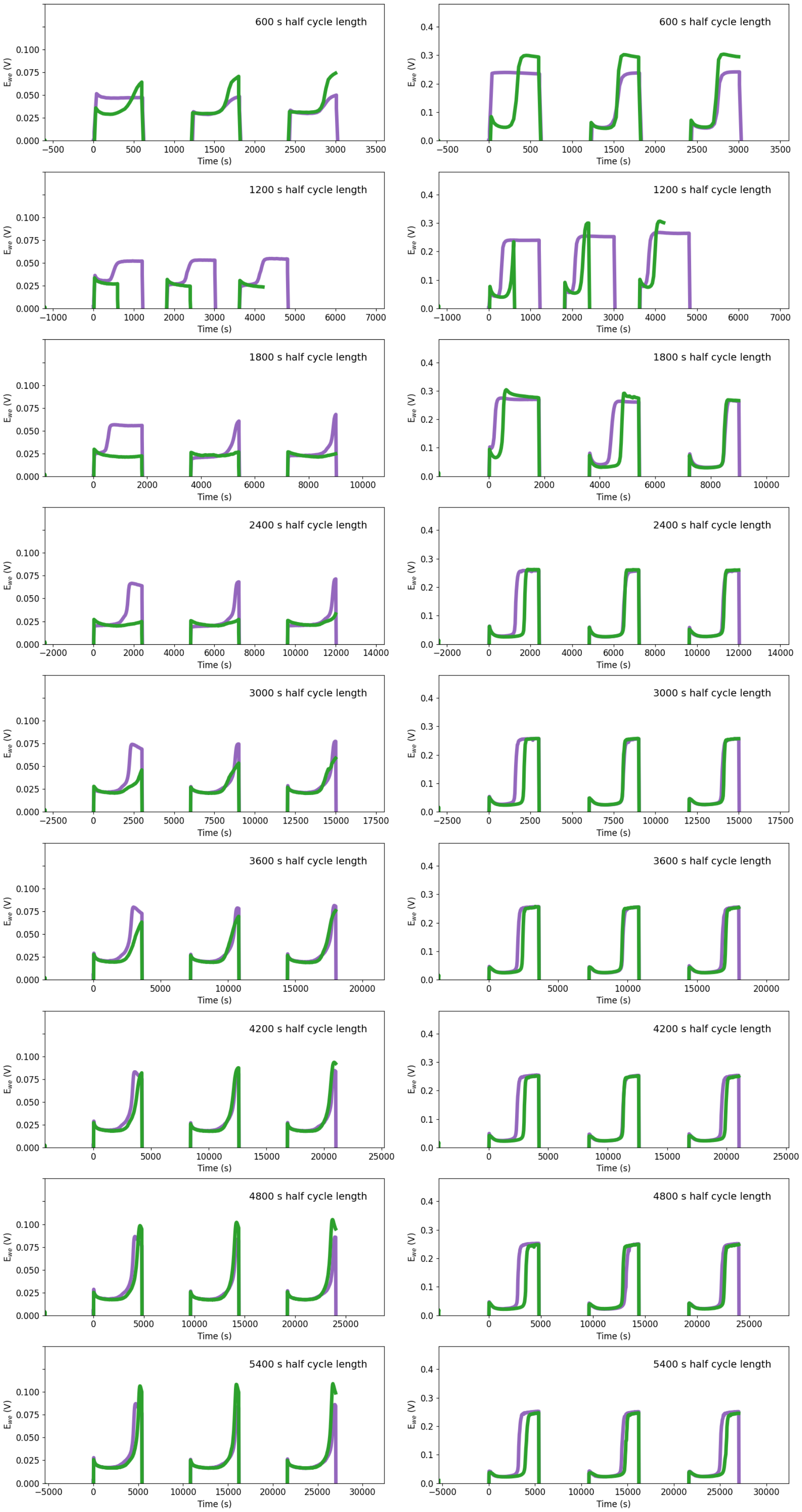

Fig. 3 Comparison of increasing half cycle time LREM symmetric cells in the two electrolytes, left LiTFSI and right $LiPF_6$ (note that the voltage scale for $LiPF_6$ is 4 times larger than LiTFSI). Electrode A (purple) is the response first half of each cycle and Electrode B (green) is the second half cycle inverted and shifted for easy comparison.

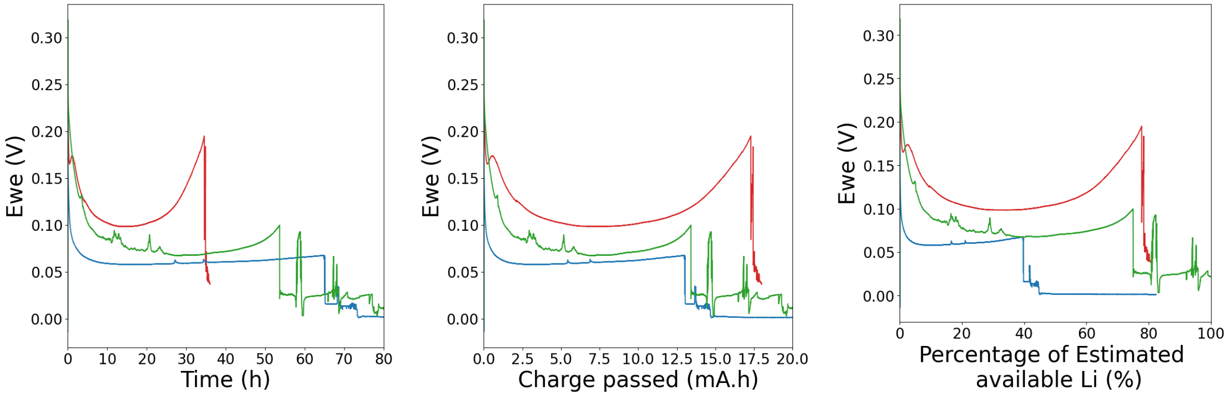

Fig. 4 Deep strip potential profile for 0.5 mA (red), 0.2 mA (green) and 0.25 mA (blue) with different xaxis to illustrate that the increase in potential during a long strip is related to the available lithium content in the electrode as well as the current.

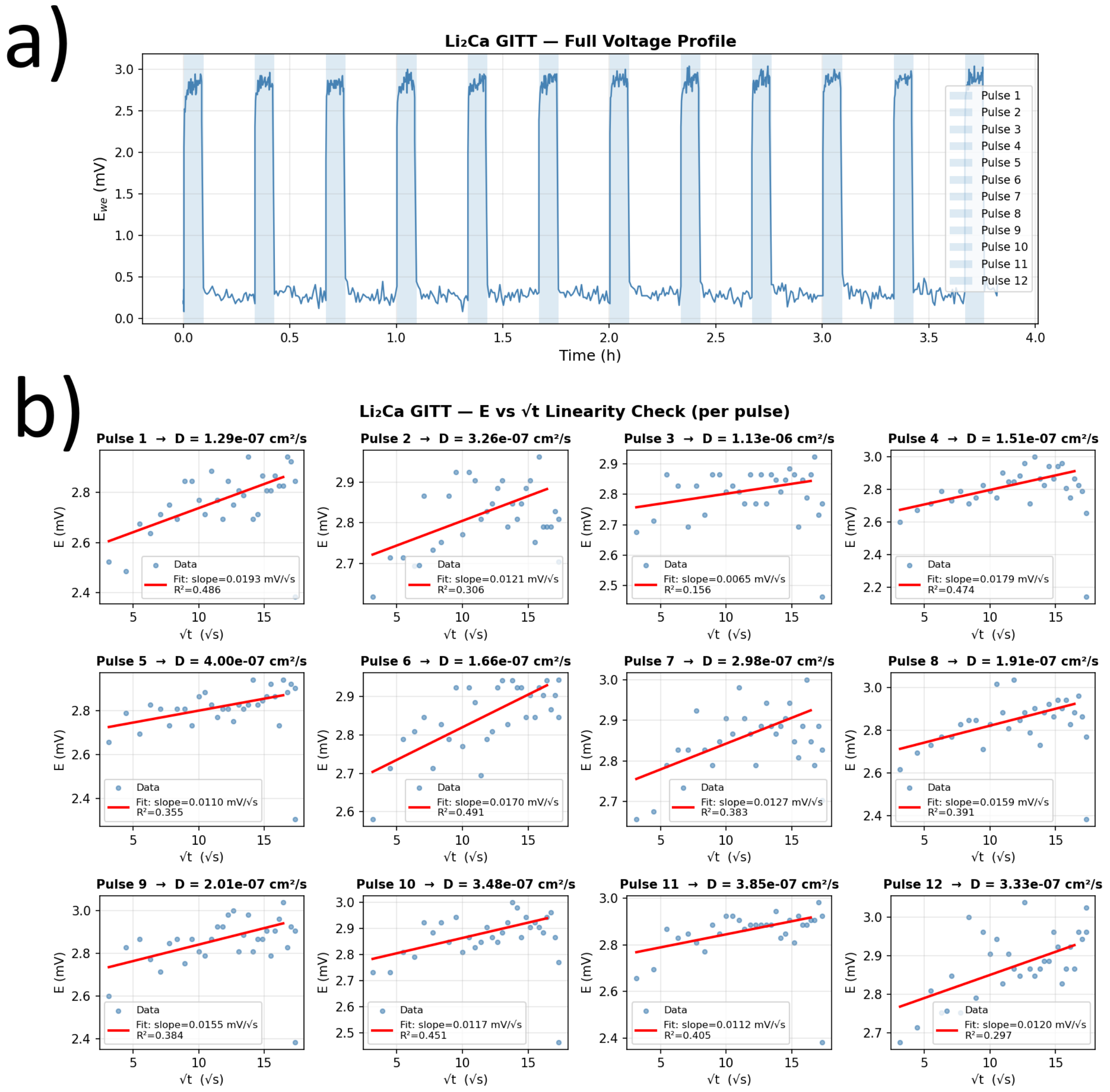

Fig. 5 a) the potential response against time for a solid-state Li_2Ca anode cast on to a stainless-steel current collector, LiTFSI electrolyte and an InLi/In counter electrode as described in Ref[?] . A pulse current density of 10 mA/g was applied for 300 s pulses, with 900 s of rest. The polarisation of the counter electrode is negligible compared to the polarisation of the working electrode. b) the fitted slope for each pulse.

Fig. 6 GITT diffusion coefficient results for Li_2Ca vs Li/Li^+.

Pulse	ΔE_τ (mV)	ΔE_s (mV)	Slope (mV/$\sqrt{s}$)	R^2	D_{slope} (cm^2/s)	D_{ratio} (cm^2/s)
1	2.304	0.180	0.01933	0.486	1.286e-07	3.133e-11
2	2.529	0.107	0.01215	0.306	3.256e-07	9.149e-12
3	2.250	0.044	0.00652	0.156	1.131e-06	1.983e-12
4	1.758	0.127	0.01786	0.474	1.507e-07	2.694e-11
5	2.090	0.069	0.01096	0.355	4.003e-07	5.536e-12
6	2.636	0.027	0.01702	0.491	1.659e-07	5.264e-13
7	2.529	0.124	0.01271	0.383	2.977e-07	1.225e-11
8	1.998	0.121	0.01587	0.391	1.909e-07	1.890e-11
9	2.132	0.030	0.01546	0.384	2.010e-07	9.989e-13
10	2.193	0.005	0.01175	0.451	3.481e-07	3.041e-14
11	2.151	0.056	0.01117	0.405	3.851e-07	3.438e-12
12	2.697	0.014	0.01202	0.297	3.327e-07	1.443e-13

Mass loading	3.01 mg
Density (Li_2Ca)	1.37 g/cm^3
Molar volume V_M	39.39 cm^3/mol
Current I	30.1 μA
Area S	2.0 cm^2

Geometric mean D_{slope}	2.809×10^{-7} cm^2/s
Arithmetic mean D_{slope}	3.381×10^{-7} cm^2/s
Geometric mean D_{ratio}	2.708×10^{-12} cm^2/s
Arithmetic mean D_{ratio}	9.268×10^{-12} cm^2/s

Fig. 7 The poor R^2 values of the slope fits in figure 5b) are illustrative of a quick transformation to a two phase system in place of a concentration gradient produced over a longer duration. This results in a smaller slope measured diffusion coefficient, therefore the ratio method is preferred as it is not biased by the two phase effect. It should be noted that a geometric surface area from the size of the sample was used in the calculation.