

Supporting Information

Exceeding 6500 cycles for LiFePO_4 / Li metal batteries through understanding pulsed charging protocols

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Section 1. Experimental Section

Open electrochemical cell

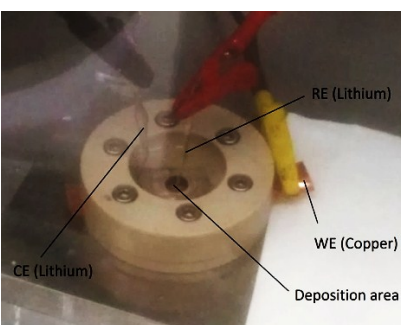


Figure S1. Photograph of the electrolyte-flooded electrochemical cell with open configuration (without separator) used for investigation of morphology changes during Li electroplating.

Scanning droplet cell

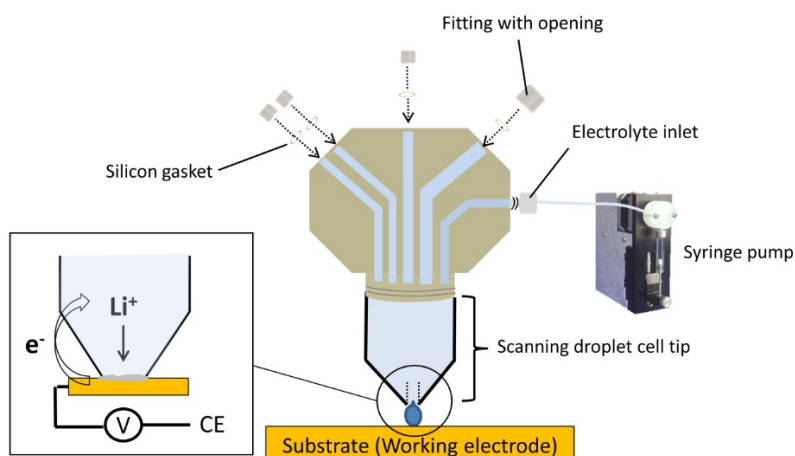


Figure S2. Scheme of the scanning droplet cell design for studying the electrochemistry of lithium in non-aqueous electrolytes. The zoom-in section shows the electroplating of lithium on the electrolyte wetted substrate area below the tip.

Section 2. Long term stability of LiFePO_4 / Li metal batteries

2.1. Battery charged by continuous galvanostatic protocol

Figure S3 shows the evolution of the specific capacity and coulombic efficiency of a LiFePO_4 / Li metal battery charged using the continuous protocol as well as the voltage profile of the last few cycles before failure.

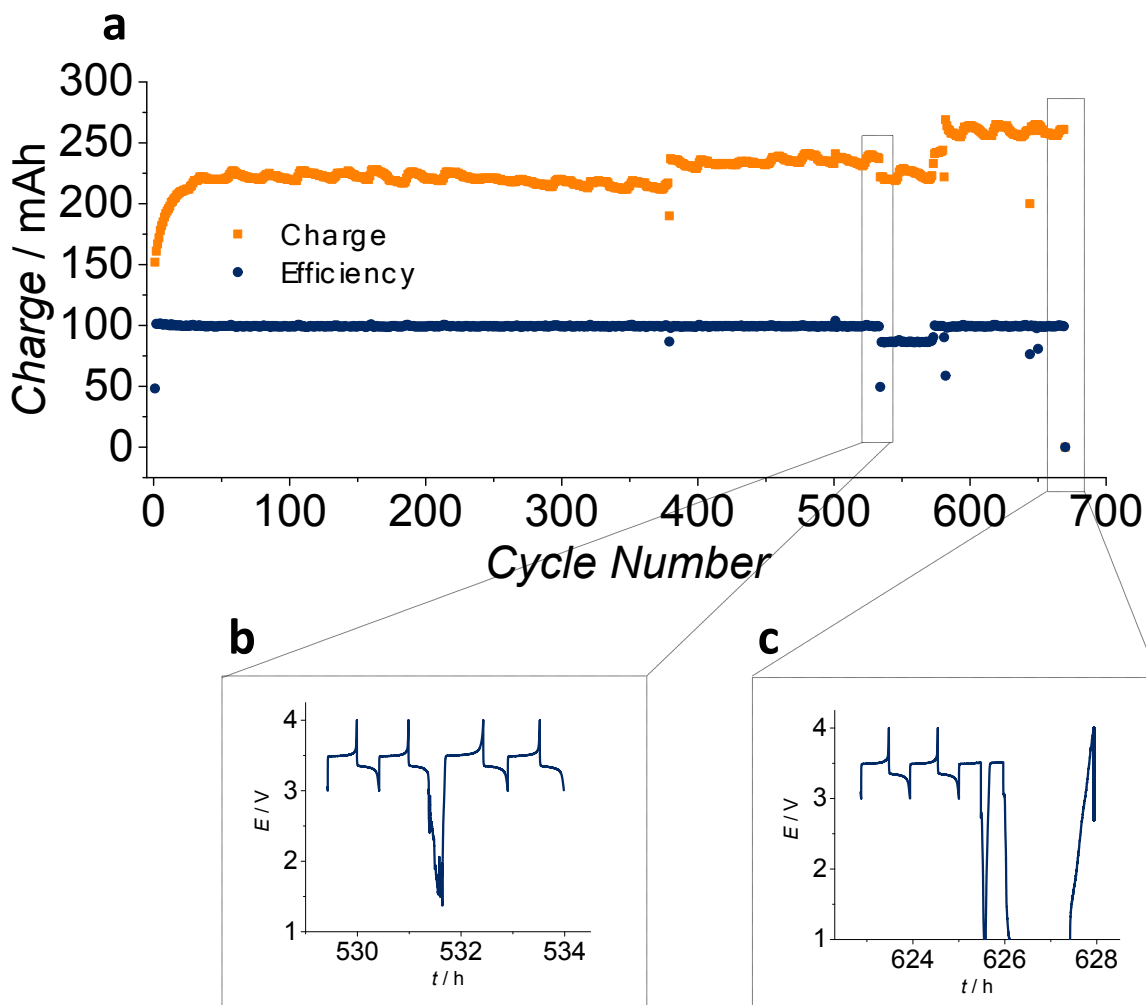


Figure S3. (a) Charge storage capacity (orange) and coulombic efficiency (blue) of a LiFePO_4 / Li metal battery upon cycling using a continuous DC charging protocol. The cell was cycled at a charge rate of 2 C (0.5 h). The electrolyte solution was composed of 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (3:7 vol.%) with 2 %wt. vinyl carbonate. Voltage profile for the cycles (b) 533-535 and (c) 669-671.

2.2. Battery charged by pulsed galvanostatic protocol.

After the failure of the LiFePO_4 / Li metal battery cycled using the pulsed protocol, the EIS spectrum (Figure S4) revealed that short-circuiting between positive and negative electrode was not the origin of the failure. The EIS spectrum showed a Warburg-type behaviour in the low frequency range which indicates that the process within this range is dominated by diffusion of Li^+ -ions, instead of obtaining a

constant value which should not contain any imaginary part and should be independent of the frequency.

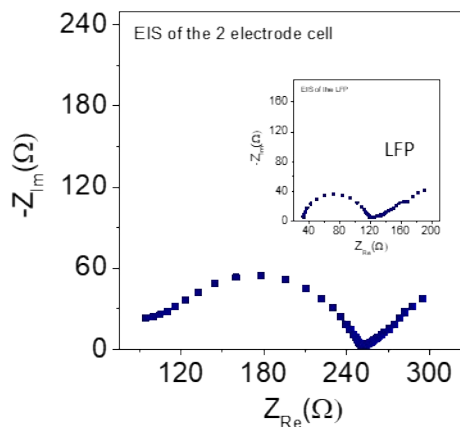


Figure S4. EIS spectrum of a LiFePO_4 / Li metal battery charged using the pulsed protocol after failure. The inset shows the EIS spectrum of the fresh cell.

After failure, the battery was still able to operate when cycled at lower charge rates indicating that the failure was not due to short-circuiting. Figure S5 shows the voltage profile of the first cycle after the failure when charged at 0.1 C. The high discharge capacity value of $150 \text{ mAh g}^{-1}_{\text{LFP}}$ indicates that the cathode material did not degrade upon cycling (even after > 6700 cycles).

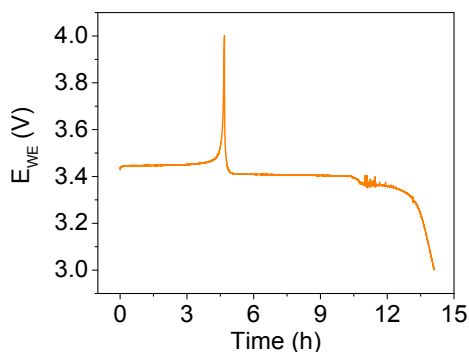


Figure S5. Voltage profile of a LiFePO_4 / Li metal battery at 0.1 C after failing after being cycled for > 6700 cycles using pulsed protocol at > 1C.

Section 3. Electrodeposition of lithium on Cu current collector

The current transients from potentiostatic measurements at different applied overpotentials (Figure S6) confirmed that short-circuit of the cell requires a lower amount of charge at higher driving forces indicating favoured dendritic growth at faster deposition rates. The transients showed that Li plating occurs under diffusion control at driving forces as low as 160 mV. Moreover, the diffusion controlled regime should be reached within a short time of a few seconds during galvanostatic Li deposition at current densities above 10 mA cm^{-2} .

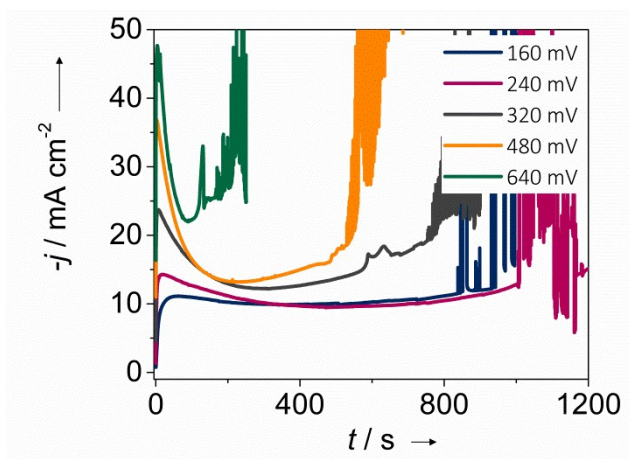


Figure S6. Current transients recorded from potentiostatic measurements of Li electrodeposition using 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (3:7 vol.%) with 2 %wt. vinyl carbonate as electrolyte. The applied overpotentials ranged from 160 mV to 640 mV vs. Li/Li^+ in 1 M Li^+ .

Section 3.1. Study using scanning droplet cell Cu electrodes

The results obtained using scanning droplet cell on Cu substrate were consistent with those gathered in the Swagelok cell. SEM images revealed that at high current densities the Li plating by the pulsed protocol resulted in smoother Li films than those obtained using the continuous protocol (Figure S7). Although the differences were not so evident when low current densities were applied (Figure S8), little changes can have a tremendous impact in the long term cyclability (>6000 cycles).

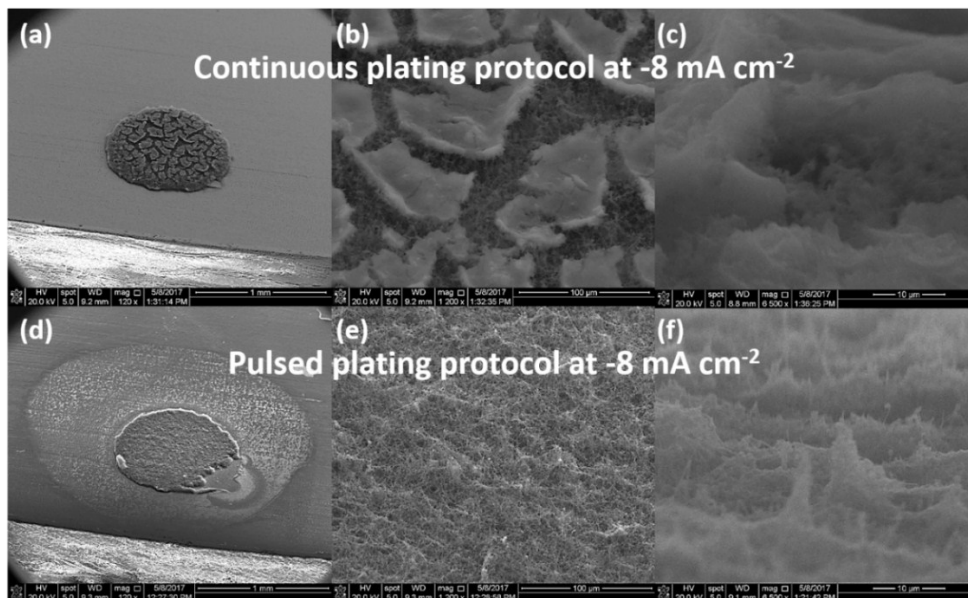


Figure S7. SEM micrographs of Li electroplated (1 mAh cm^{-2}) on a Cu foil current collector at -8 mA cm^{-2} using the scanning droplet cell. The electrolyte solution consisted of 0.5 M LiPF_6 (Novolyte) in propylene carbonate (anhydrous, Sigma Aldrich®). Samples prepared by (a), (b) and (c) continuous and (d), (e) and (f) pulsed (2s/1s ON/OFF) plating protocols. (a) and (d) are top views with magnification of 120 times, (d) and (e) are top views with magnification of 1200 times, and (c) and (f) are tilted-views (*ca.* 70°) with magnification of 6500 times.

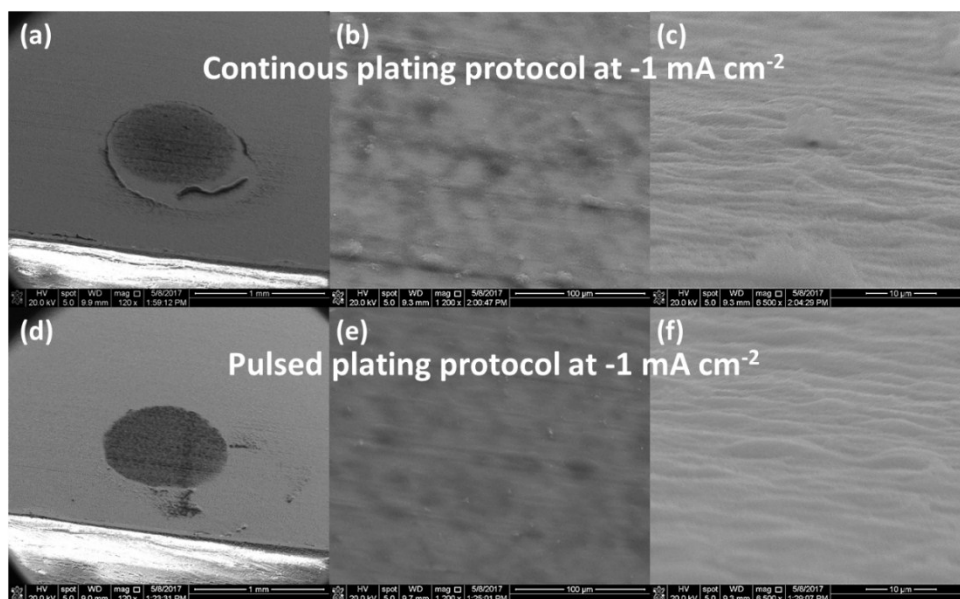


Figure S8. SEM micrographs of Li electroplated (1 mAh cm^{-2}) on a Cu foil current collector at -1 mA cm^{-2} using the scanning droplet cell. The electrolyte solution consisted of 0.5 M LiPF_6 (Novolyte) in propylene carbonate (anhydrous, Sigma Aldrich®). Samples prepared by (a), (b) and (c) continuous and (d), (e) and (f) pulsed ($2\text{s}/1\text{s ON/OFF}$) plating protocols. (a) and (d) are top views with magnification of 120 times, (d) and (e) are top views with magnification of 1200 times, and (c) and (f) are tilted-views ($\text{ca. } 70^\circ$) with magnification of 6500 times.

Table 1 shows the values of the coulombic efficiency of the Li plating / stripping cycle on the Cu current collector for continuous and pulsed protocols at different current densities. At high current densities, pulsed plating protocols mitigated the drop in coulombic efficiency, which can be further improved (table 2) by optimizing the pulsing parameters such as duration of pulse and resting period. It should be note that this study aim at elucidating trends since the actual values would change when changing the electrode from Cu to Li.

Table 1: Comparison of the average coulombic efficiencies obtained with continuous and pulsed galvanostatic plating protocols ($0.167 \text{ mAh cm}^{-2}$) at different current densities. All values were averaged over three samples.

Plating current density [mA/cm ²]	Coulombic Efficiency Continuous	Coulombic Efficiency Pulses
-0.5	83.1 % $\pm$ 0.9 %	83.3 % $\pm$ 0.8 %
-1	81.8 % $\pm$ 0.9 %	81.1 % $\pm$ 0.5 %
-2	83.7 % $\pm$ 0.1 %	83.6 % $\pm$ 0.4 %
-4	63.9 % $\pm$ 0.9 %	72.4 % $\pm$ 1.1 %
-8	60.7 % $\pm$ 0.3 %	61.7 % $\pm$ 0.5 %

SEM images and coulombic efficiency measurements suggest that pulsed plating protocols at high current densities lead to the formation of smoother Li films which in turn results in higher coulombic efficiencies.

Table 2. Comparison of the coulombic efficiencies obtained with pulsed galvanostatic plating protocols at -8 mA cm^{-2} with different duration of the pulse at a fixed relaxation time of 0.5 s.

Pulse duration	Coulombic Efficiency
1 s	54.2 %
0.5 s	60.5 %
0.25 s	64.7 %
0.125 s	72.9 %

Section 4. Electrodeposition of lithium on Li metal electrodes

Section 4.1. Study using scanning droplet cell

The impact of charging protocol and the porous film on the resistance of the Li metal electrodes was evaluated by EIS measurements. No significant differences between continuous and pulsed protocols were observed after 10 cycles. For longer cycling, the charge transfer resistance increased only slightly ($10 \Omega \text{ cm}^2$) after 100 cycles for the pulsed protocol, whereas the resistance increased to $40 \Omega \text{ cm}^2$ after only 30 cycles when cycled using the continuous protocol.

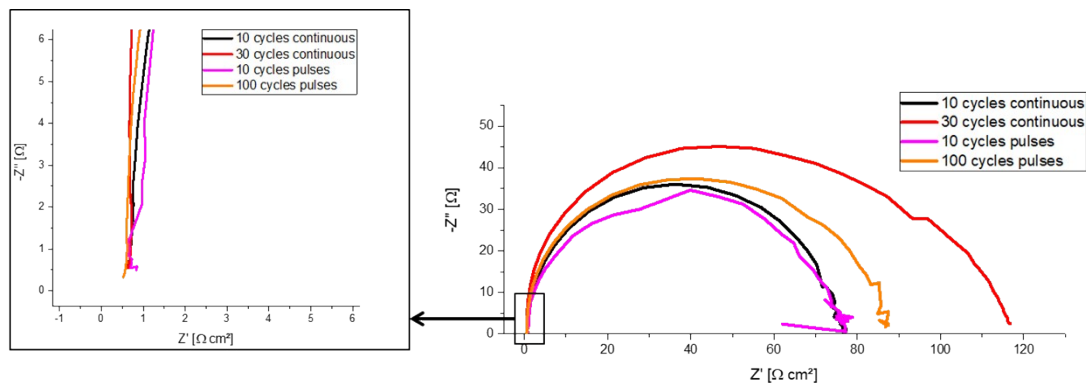


Figure S9. Evolution of EIS spectra upon cycling using continuous and pulsed protocols. The inset shows a magnification of the high frequency region.