

## Degradation of Al Current Collector in Lithium-Ion Batteries Using Liquid Phase Electron Microscopy

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Lithium-ion batteries (LIBs) are the state-of-art rechargeable, secondary batteries. Their use in portable devices and electric vehicles (EVs) make this type of battery of particular interest[1–3]. More specifically, with the ongoing growth of the EVs market, driven by the global tendency aiming toward the decrease of fossil fuel consumption[1, 3], the improvement of the current LIBs technology is required, and more particularly their performance, their safety and their lifetime[1, 3, 4]. The research in this domain has mainly been focused on electrodes and electrolyte optimization. However, the role of the current collectors on the LIBs performance is nowadays poorly understood[5]. Because of the intrinsic complex and interlinked chemistry of LIBs, a deconvolution of all effects can provide valuable insights on the mechanisms of their degradation.

In bulk devices, the current collector on the cathode side is aluminum due to its low price and good electric conductivity[3]. This material presents a good corrosion resistance at cathodic conditions with the formation of passive layers in contact with the non-aqueous electrolyte[1]. However, its corrosion is still possible and is influenced by several key parameters: the potential, the electrolyte composition, the coating of the current collector and its microstructure[3, 5]. The exact mechanism of the Al current collector corrosion and its implication on the whole LIB cell are yet not fully understood[3, 5]. To understand the impact of the degradation of the Al current collector on the performance of LIB, we use liquid cell transmission electron microscopy (LCTEM), which allows to perform and observe dynamic experiments in the liquid phase[6]. This technique is enabled by using specific TEM holders that are enclosing liquid solution between two micro-electromechanical systems (MEMS) chips. On one of these chips, electrodes can be patterned and electrically biased for performing *in situ* or *operando* electrochemical experiments.

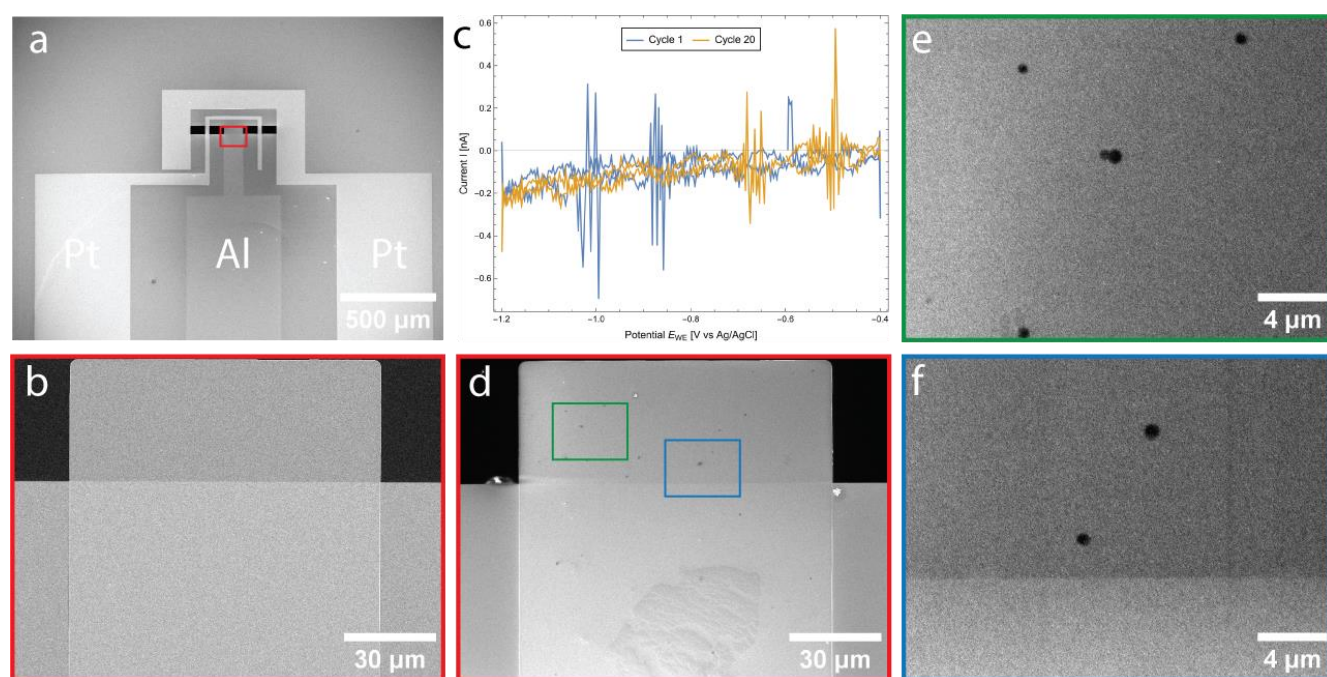
In this paper, we report the development of in-house microfabricated MEMS chip that includes a 50 nm thick Al WE and two 50 nm thick Pt electrodes that were lithographically patterned and e-beam evaporated on a 50 nm SiN<sub>x</sub> membrane (Fig. 1a&b). Preliminary cyclic voltammetry (CV) experiments in 0.1 M NaCl solution (>99.5%, Carl Roth) were performed on the bench using a Pt wire as counter electrode and a Ag/AgCl reference electrode. The Al WE was biased between -1.2 V and -0.4 V vs Ag/AgCl for 20 cycles with a scan rate of 10 mV/s using a potentiostat with ultralow-current probe (Bio-Logic SP-300). The CV curves for the 1st, and 20th cycles are depicted in Fig. 1c. The curves show a stable behavior for 20 cycles, with the current oscillating between -0.25 and 0.1 nA while potential cycling. The larger peaks observed for the depicted cycles are due to external noise occurring during the experiment. Post-mortem analysis of the chip (Figs. 1d-f) indicates darker spots on the Al WE, which correspond to the location where initial stage of pitting corrosion of the Al WE is occurring, in agreement with previous studies[7]. By increasing the number of cycles, the density of such pitting hole is expected to increase.

The aluminum current collector degradation as function of applied potential and electrolyte composition

will be discussed. Further work on *in situ* observations of its corrosion will aid towards understanding its implication on LIB performance.

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**Figure 1.** a) SEM image of in-house microfabricated LCTEM chip with Al WE and two Pt electrodes. Red rectangle corresponds to the area shown in b and d. b) SEM image of the Al WE before CV experiments. c) CV curves of 1st and 20th cycles. d) SEM image of the Al WE after the CV experiments. Green and blue rectangles are corresponding to the localization of e, and f, respectively. e,f) SEM images of corroded region on the Al WE.