

## Memory effect highlighting in silicon anodes for high energy density lithium-ion batteries

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Because of its high theoretical specific capacity ( $3579 \text{ mAh.g}^{-1}$  or  $834 \mu\text{Ah.cm}^{-2}.\mu\text{m}^{-1}$  until the  $\text{Li}_{15}\text{Si}_4$  composition) [1] and its low working potential, silicon is intensively studied in order to enhance the energy density of Li-ion cells and to replace graphite as negative electrode for specific applications. But this high capacity implies large volume change ( $> 280\%$  in the bulk form) which constitutes a starting point of various problems, leading to a relatively fast capacity fading of composite electrodes in liquid electrolytes [2]. Sputtered silicon thin film electrodes are far less sensible to this volume change, and show better capacity retention than silicon-based composite electrodes [2, 3]. In addition, side reactions with conventional carbonate-based electrolytes are minimized by the addition of a passivating agent (like VC or FEC for instance) [3, 4]. Then, this configuration allows achieving a good cycle life and getting more direct information on the silicon electrochemical response, avoiding any parasitic effects or limitations which could be due to binders or conducting additive materials.

This work presents a special feature of silicon electrodes, never reported up to now to our knowledge, called “memory effect” in reference to the Ni-Cd technology. As a reminder, this effect implies an artificial capacity fading in Ni-Cd batteries when the cell is not fully discharged before charging [5]. A similar effect was revealed on silicon electrodes when cycled at low potential in a reduced voltage range, corresponding to the formation of Li-rich silicon alloys. In other words, if a lithiated silicon electrode is not reoxidized (delithiated) deeply enough, the subsequent lithiation is then less effective than the previous one.

This memory effect was highlighted by galvanostatic and potentiostatic characterizations on silicon thin film electrodes, with various thicknesses and under several electrochemical conditions (discharge cut-off potential and duration of floating) [6]. It turns out that memory effect only occurs if the mean amount of inserted lithium is high enough. Then a progressive loss of capacity is observed over cycling correlated with an evolution of the voltage profile leading to a less and less efficient Li extraction and insertion. This phenomenon was clearly highlighted when the crystallized phase  $\text{Li}_{15}\text{Si}_4$  is formed, but also for Li-rich compositions even in absence of  $\text{Li}_{15}\text{Si}_4$ . Although this loss of capacity is fully reversible after a deep oxidation of the  $\text{Li}_x\text{Si}$  electrode, it can be avoided by an appropriate balancing of the positive and the negative electrodes in the full Li-ion cell.

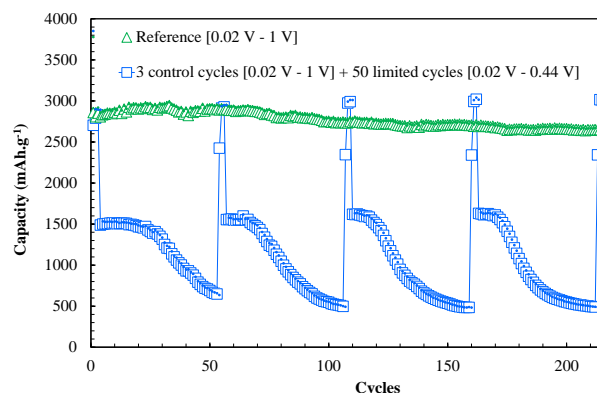


Figure 1: Evolution of the capacity for 100 nm thick electrodes cycled either in a sequence including 3 control cycles followed by 50 limited cycles, or only in a wide potential window (reference)

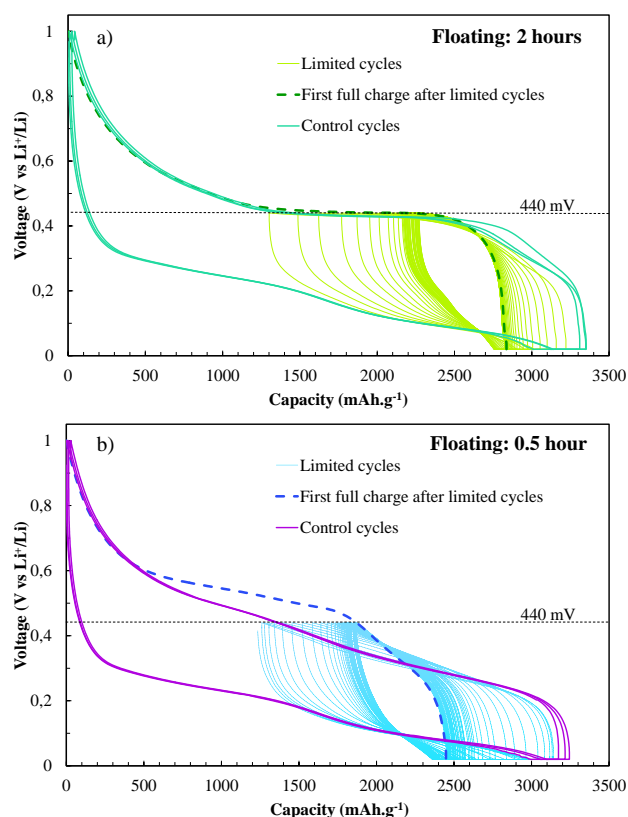


Figure 2: Evolution of the electrochemical profiles of 400 nm thick Si thin film electrodes for a) 2 hours and b) 30 min floating duration at the end of the discharge.

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