Selection and optimisation of silicon anodes for all-solid-state batteries

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In the field of energy storage, Lithium-ion (Li-ion) technology is currently the most widespread on the market. It is widely integrated in portable electronic devices and is gaining interest in the automobile sector due to the development of electrical vehicles. However, its performance are reaching its limits. Solid-state Li-ion battery (SSB) is a very promising technology for next generation energy storage devices due to the promise of higher energy densities and its enhanced safety [1]. SSB are expected to enable a safe use of lithium metal anodes. However, high reactivity of lithium metal with solid electrolyte lead to fast degradation of performances. Another issue is the dendrite growth during cycling [2]. Consequently, silicon has been identified as a promising anode material alternative. Its great abundance, its reasonable working potential of 0,4V vs Li/Li^+ and its high theoretical specific capacity of 3579mAh/g are its main advantages. However, due to the formation of an alloy with lithium ions up to the $Li_{15}Si_4$ phase, the silicon will undergo a strong volume expansion of almost 300%. Various techniques are described in the literature to limit this phenomena mainly with liquid electrolytes, such as the use of nano-sized silicon particles [3]–[5]. Moreover, the reactivity of silicon with the solid electrolyte is little studied in all solid-state batteries. In this work, the cyclability and the reactivity of two different silicon materials with sulphide-based solid electrolyte was studied. The silicon materials studied have a different morphology: one is made of commercial micrometric silicon particles (SiMicro) (2-10µm) and the other is silicon nanowires (SiNWs) (10nm) synthesized in the laboratory by a chemical growth process [6].

The silicon-based composite consists of 30wt% silicon, 50wt% solid electrolyte (Li_6PS_5Cl) and 20wt% conductive additive (VGCF). The different powders are mixed by manual grinding for 15 minutes. To study the effect of composite ageing, composite are either used directly for electrochemical characterisation (Fresh Composite) or after a few weeks of storage in the glove box (Aged Composite). The entire cell manufacturing process is carried out in a glove box.

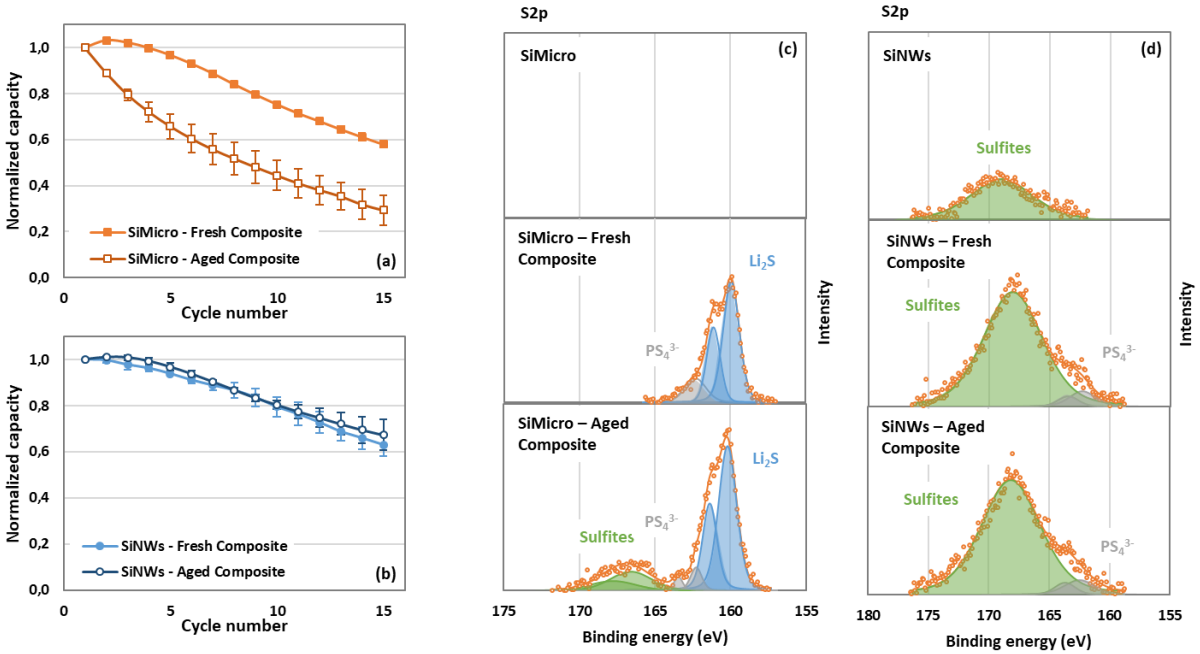

Figure 1. Cycle performances of half cells with new and aged (a) SiMicro-LPSCl-VGCF composite anodes and (b) SiNWs-LPSCl-VGCF composite; (c) S2p XPS spectra of SiMicro, new composite SiMicro-LPSCl-VGCF and aged composite SiMicro-LPSCl-VGCF; (d) S2p XPS spectra of SiNWs, new composite SiNWs-LPSCl-VGCF and aged composite SiNWs-LPSCl-VGCF

Normalized capacity as a function of the number of cycles for composites of SiNWs and SiMicro with and without ageing is shown in Figure 1 (a – b). The first striking result is the difference in composite ageing between SiNWs and SiMicro. Indeed, the aged composite causes a strong degradation of the cycling stability for SiMicro compared to the new composite, with 30% of the initial capacity at the 15th cycle versus 60%. On the contrary, no difference is observed for SiNWs between the two types of composites. It is therefore possible to assume that SiMicro has a higher reactivity with the solid electrolyte than SiNWs. To understand what species are formed during storage of the composite and why SiMicro is more reactive than SiNWs in the composite electrode used, XPS analyses were performed. First the raw materials were analysed, then the composite powders with and without ageing. The largest differences between the different powders could be observed with the S2p spectrum presented in Figure 1 (c – d). The presence of sulphur on the nanowires can be explained either by the synthesis conditions or by the storage in a sulphur glove box. The elements observed on the S2p spectrum are therefore very different depending on whether the composite is made with SiMicro or SiNWs because of the difference in the materials alone. With regard to the ageing of the composite powder, the spectra obtained are identical for SiNWs before or after ageing, whereas an evolution is observed with SiMicro. Indeed, a characteristic doublet of oxidised sulphur appears after ageing. It is therefore possible to observe by XPS a degradation of the electrolyte for SiMicro, which is in agreement with the electrochemical characterizations. Future work will involve modifying the surface of SiMicro to compare with the surface of SiNWs obtained after synthesis.

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