An Agglomeration Mechanism and a Protective Role of Al_2O_3 for Prolonged Cycle Life of Si Anode in Lithium-ion Batteries

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Si, the high-capacity anode for Li-ion battery (LIB), has intrinsic 300% volume changes limiting its commercial application. The volume change leads to particle pulverization that result in loss of electrical contacts. Various nanostructures are proposed to avoid the pulverization, but the commercialization is still a distant future. Recently, Al_2O_3 has demonstrated its ability to enhance electrochemical cycling performance. However, a comprehensive mechanistic role of the Al_2O_3 has not been well understood. Here, we have combined electrochemical and chemical agitation test to propose two novel mechanisms: Si agglomeration and a protective role of the Al_2O_3 (**Figure**). $LiPF_6$, the common Li salt of the LIB electrolyte, decomposes and form HF that etches the native oxide layer then form labile Si-H surface. Because of the labile Si-H surfaces, the Si particles agglomerate during the volume changes. The Si agglomeration has a detrimental effect on the cycling performance associated with the loss of electrical contacts. On the other hand, in the presence of the Al_2O_3, the Al_2O_3 consumes the HF, protecting the native oxide layer that resists the agglomeration. Thus, the Si particles with Al_2O_3 are better dispersed. The Al_2O_3 allows the better Si dispersion during electrochemical cycles, resulting in improved capacity retention.

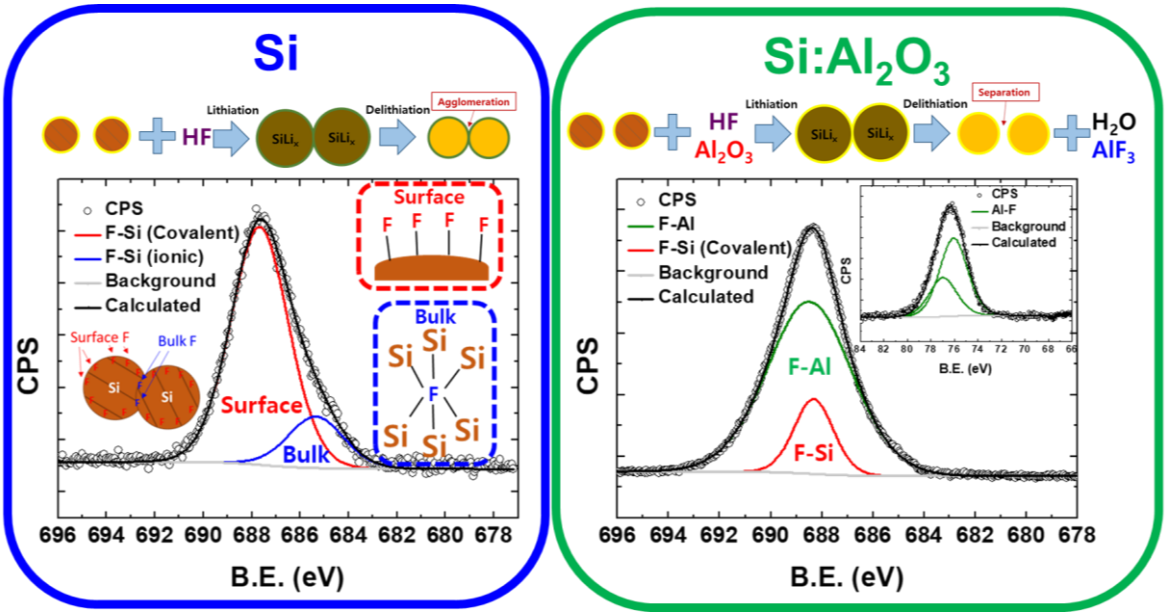

Figure: Schematic illustration of the Si agglomeration mechanism with the evidence of F-Si bulk species (Left). Schematic illustration of the protective role of Al_2O_3 with the evidance of F-Al species (Right).