Robust Si Anode Design for Li-ion Battery on Polyimide Substrate: Villus-Like Polymer/Si Core/Shell Hybrid Nano-structure

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Polymer substrate based devices for the next-generation electronics will open the new era, enabling to have excellent advantages: more lightweight, bendable, disposable and cost effective. Among these polymer substrates, polyimide (PI) has been widely used for polymer based devices in aerospace, telecommunications, medical and general electronics due to the excellent thermal stability, stable mechanical properties and good chemical resistance compared to other polymer substrates. For the upcoming electronics such as RFID tag, smart chip card, an imbedded energy storage device is inevitably needed. However, PI based energy storage devices have been rarely developed. In this work, we fabricated a new PI substrate based Li-ion batteries with nanostructured Si anode for next generation polymer substrate based electronic devices. According to current fashion of miniaturization and high integration of disposable and lightweight electronic devices, we tried to utilize high capacity anode material. In many of active anode materials, Si is chosen as very attractive and promising candidate owing to its theoretically huge gravimetric and volumetric capacity. Si, however, shows severe mechanical degradations (crack, delamination) on the thin film electrode due to the huge volume expansion upto 300% during lithiation process. To overcome this limit, we suggest a nano-hairy polymer/Si core/shell hybrid structure via the directly fabricating nanostructured PI on the substrate which is called villus-like nanostructured Si anode. We designed our nanostructured Si electrode by focusing the following two criteria: how to design the effective structure to improve the mechanical stability from the Si volume expansion and how to increase the effective surface area in the limited space to maximize the exellent rate capabilities. To demonstrate these aims of research, we performed the *in-situ* lithiation test and electrochemical measurement using coin cells.

We fabricated widely and densely distributed nano-hairy PI on the PI substrate through the dry etching process using CF_4 gas. The diameter and height of nano-hair is approximately 100 nm and 1 ㎛, respectively as shown in Fig 1 (b) from pristine PI in Fig. 1(a). For the current collector and active material, Cu layer (200 nm) and Si (300 nm) was deposited on the nano-hairy PI substrate using thermal evaporation method. To compare the performance of the anode characteristics, pristine PI substrate was introduced. Through the *in-situ* lithiation test, we elucidated the characteristic lithiation behavior of nano-hairly Si anodes: the isotropic volume expansion accommodated by compliable movement and free space. Followed by the coin-cell test performed from 0.01 V to 2.00 V (versus Li/Li^+), we proved that our design dramatically improve capacity, cycle life and rate capabilities compared to the thin film Si anode on the pristine PI because this hybrid nanostructured Si anode effectively suppressed mechanical failures such as buckles and delamination. Subsequently, we maximized surface area by reducing the size of nano-hairs down to 20-30 nm by changing the different gas atmosphere for the further progress in Fig. 1(c). According to the high rate charge/discharge test, thinner nano-hairy structure showed better performing capacity behavior on various C-rate steps as indicated in Fig. 1 (d). It is considered that increased effective surface area and free space provided the more Si to react and buffering effect from the Si volume expansion. Detail mechanism of this result will be also discussed. Our novel design concept of Si anode on the PI substrate will open the new possibility of imbedded energy storage for next generation PI based electronic devices.

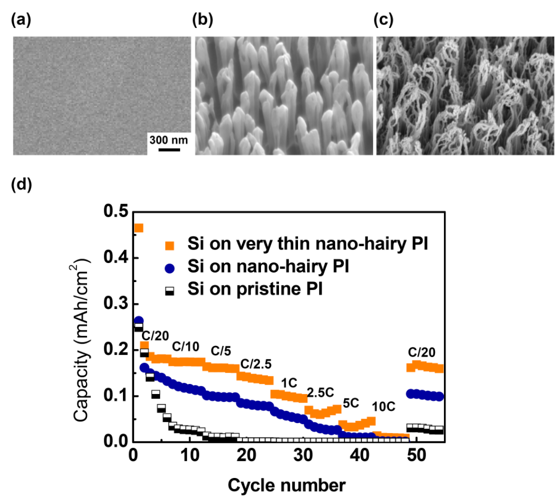

Fig. 1 (a) Prinstine PI (b) villus-like nano-hairy PI etched by CF4 gas (c) Very thin nano-hairy PI etched under different gas atmosphere (d) rate capability test on various form of PI substrate