



# Double-plasma enhanced carbon shield for spatial/interfacial controlled electrodes in lithium ion batteries via micro-sized silicon from wafer waste



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## HIGHLIGHTS

- A micro-sized Si source from residual waste without complicate chemical synthesis.
- A distinct surface modification to modify the status of interface.
- A viewpoint of materials' interface to suppress the formation of SEIs.
- An enhanced performance via modifications from the internal to external electrode.

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## ABSTRACT

Using spatial and interfacial control, the micro-sized silicon waste from wafer slurry could greatly increase its retention potential as a green resource for silicon-based anode in lithium ion batteries. Through step by step spatial and interfacial control for electrode, the cyclability of recycled waste gains potential performance from its original poor retention property. In the stages of spatial control, the electrode stabilizers of active, inactive and conductive additives were mixed into slurries for maintaining architecture and conductivity of electrode. In addition, a fusion electrode modification of interfacial control combines electrolyte additive, technique of double-plasma enhanced carbon shield (D-PECS) to convert the chemical bond states and to alter the formation of solid electrolyte interphases (SEIs) in the first cycle. The depth profiles of chemical composition from external into internal electrode illustrate that the fusion electrode modification not only forms a boundary to balance the interface between internal and external electrodes but also stabilizes the SEIs formation and soothe the expansion of micro-sized electrode. Through these effect approaches, the performance of micro-sized Si waste electrode can be boosted from its serious capacity degradation to potential retention (200 cycles, 1100 mAh/g) and better meet the requirements for facile and cost-effective in industrial production.

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## 1. Introduction

In recent years, the awareness of environmental protection and sustainability has increased the urgency to develop renewable resources from waste and green energy.[1–4] Solar energy, which converts pure natural light into a usable energy source, is advertised as a solution of replacing petroleum but in turn produces tons of waste during the cutting wafer fabrication process, namely kerf loss wafer slurry waste [5–8]. This slurry contains micro-sized

silicon (Si), silicon carbide, and slicing fluid contaminants. After chemical purification and physical separation, the recycled waste was selected as a low-cost and efficient material for Si-based anodes of energy storage devices – lithium ion batteries (LIBs) [9–12].

With the theoretical capacity of alloyed Si nearly 3590 mAh/g, Si is recognized as a favorite research topic with the potential to take over the market of conventional carbon anode. Nevertheless, the three-fold volume expansion caused by alloy formation (i.e. lithiation) is a serious drawback and can lead to structural pulverization [13–15]. Lithiation process of Si is accompanied by the expansion and contraction of silicon during the operation of voltage window, promoting the interaction between the Si-based electrode and the electrolyte and the decomposition of electrolyte. This

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process creates insulating solid electrolyte interphases (SEIs) that drains the capacity of the battery with each cycle [16–22].

With the purpose to achieve long duration with high capacity, nanostructured Si particles with peculiar architecture via complicated chemical synthesis are usual solutions for maintaining the stabilization of electrodes and isolating silicon particles to react with electrolyte [21–25]. In the other words, the spatial control in the electrode and interfacial control between active materials and electrolyte are both critical issues to enhance the performance of Si-based anode. However, the process of shrinking particle size of Si to keep the capacity retention involves complicated chemical syntheses with acid etching, catalysis and expensive vacuum devices to achieve above mentioned criteria [26–37]. Otherwise, the present Si-based anode generally requires expensive cost and consumed time for nanolizing process, which is absolutely far away from the demand of mass production for industry. Except for the common strategies of designed particles structure, KS6 and Fluoroethylene Carbonate (FEC), are used commonly as additives in electrode and electrolyte, respectively. The flake carbon black, KS6, supplies a conductive route to interlink the isolated particles within the spatial control in the electrode. FEC provides the effect to turn a porous SEIs layer into a smoother and more stable structure via the interfacial control in the electrolyte [38–40]. Both additives offer the purpose to stabilize the as-prepared electrode. To be worth mentioned, the selected waste material in this study, the micro-sized Si, is ten times larger and much cheaper than conventional nanostructured-Si. Due to its particle diameter is exceeded the critical size (~250 nm) to produce more pulverization of Si and deterioration of electrode, the selected Si waste (~several micrometers) is suffered inevitably from unavoidable fractures and severer SEIs formation during cycling to influence in the stability of electrode [41–45]. Therefore, the spatial and interfacial control for the stability of electrode are a more rigorous challenge for the case of wafer waste.

In order to keep the synthesis away from complicatedly chemical processes or costly vacuum equipment and also enhance the cyclability of recycled waste, the extracted resource based electrodes were modified step by step via the spatial control of active/inactive/conductive additives followed by the interfacial control of internal/external electrode modification. As the presented results show, general methods for nanostructured Si by mixing conductive and electrolyte additives can only prolong the retention slightly and is unable to be applied as the solution for the case of recycled waste. Hereby, a unique and integrated modification, double-plasma enhanced carbon shield (D-PECS) was introduced to exert over the surface of electrode, combining the technology of atmospheric pressure plasma jet (APPJ) and evaporation coating (EC). This innovative fusion of surface modification can preserve the tranquility of the interface of electrode and electrolyte by the existence of Li–N. Despite the undercurrent of severe particle expansion inside the electrode during lithiation, this converted interface stabilizes the continuous formation of SEIs at the beginning of cycling. Finally, after the gradual tuning of spatial and interfacial control, the modified recycled waste is shown to be a promising material for the manufacture of low-cost and efficient anodes in the application of LIBs.

## 2. Experimental

### 2.1. Recycled waste from wafer slurry

The recycled waste was extracted from the wafer slurry during the cutting process of silicon wafer in solar-related factories. At the beginning, the slurry contains particles of silicon (Si), silicon carbide, and slicing fluid contaminants. After chemical cleaning and

physical separation, micrometer-sized Si and SiC can be obtained individually as the active and inactive materials. The as-prepared powder after purification process is supplied by Chan Ann Company Limited (Taoyuan, Taiwan). For the electrode fabrication with different stages of spatial and interfacial control, the Super-P and sodium alginate (SA) were selected as essential ingredients as carbon blacks and binder for the purposes of conductivity and adhesion. The spatial and interfacial controlled electrodes were assembled into a coin cell (CR2032) in an Ar-filled glovebox containing a counter electrode (Li metal), separator (porous polypropylene), and electrolyte (1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate = 1:1 with and without 5 wt% FEC) for the electrochemical measurement.

### 2.2. Spatial control and interfacial control for the electrode within micro-sized Si waste

In the stage of spatial control (SC), the active, inactive and conductive additives are mixed step by step as the electrode stabilizers to compose the slurries of waste-based electrodes. The active, inactive and conductive additives are using Si, SiC and KS6 (graphite flakes, Aldrich), namely as Si<sub>space</sub>, SiC<sub>space</sub> and KS6<sub>space</sub>, respectively. After a series of spatial control, a common electrolyte additive, Fluoroethylene Carbonate (FEC, Aldrich), is used as an internal agent to suppress the formation of SEIs between particles. In addition, a unique process, double-plasma enhanced carbon shield (D-PECS), is applied onto the surface of spatial controlled electrode as an external agent to modify the surface bonding states. Finally, a fusion modification is introduced to combine FEC and D-PECS for boosting the performance of waste-based electrode. The interfacial control of internal, external and fusion modifications are named as FEC<sub>interface</sub>, D-PECS<sub>interface</sub> and F&D<sub>interface</sub>, respectively. The detailed parameters are listed in Table 1. Noticeably, the weight of calculated specific capacity is marked specially with orange occupied area in Fig. 1 and Table 1. Si, SiC and KS6 are counted into the exact weight for both cases in spatial and interfacial stages to emphasize the contribution of active, inactive and conductive effect for waste-based electrode.

### 2.3. The process of double-plasma enhanced carbon shield. (D-PECS)

A unique process of interfacial control firstly applied onto the surface of spatial controlled electrode to modify the chemical bonding states. Such surface modification integrates the technologies of atmospheric pressure plasma jet (APPJ) and evaporation coating (EC) with an interlocked sequence. At first, the micro-sized Si electrodes were treated by the APPJ once (pre-plasma) then a carbon (C) overlayer was evaporated onto the electrode following the APPJ treatment (later-plasma) again. Such surface modification constructed by a plasma-assisted electrode with plasma enhanced C overlayer as shown in Fig. 1, named as Double-Plasma Enhanced Carbon Shield (D-PECS) in this study. The APPJ device was designed with a tungsten rod as the electrode surrounded by a grounded stainless steel nozzle. The 13.56-MHz rf power supply was coupled with an automatic matching box for applying 50 W power and a composed gas flow of high purity argon (99.99%, 15 slm) and nitrogen (99.99%, 40 sccm). The APPJ treatment was exerted over the surface of micro-sized Si electrode on a X-Y moving platform with 3 mm vertical distance to plasma electrode. The EC machine used a JEOL Smart Coater with a C rod of 3 mm diameter for 6s evaporation process.

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