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# Bridging porous Si–C composites with conducting agents for improving battery cycle life

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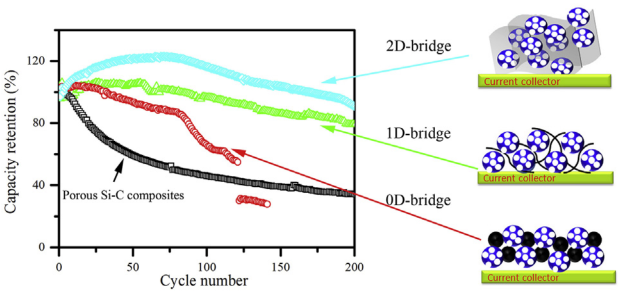
## HIGHLIGHTS

- Porous Si–C composites were fabricated by a facile sacrificing method.
- Cycle life can be greatly improved by building 0D, 1D and 2D electrical bridges.
- The capacity reaches 800 mAh/g for 220 cycles in rGO bridged electrode.
- The content of porous active materials can be kept at as high as 80%.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Porous silicon–carbon (Si–C) composites have been considered to be one of the most effective architectures to improve the cycle life of Si based anode because of its native ability to accommodate the large volume change during discharge/charge process. It is found that lots of reported porous Si–C electrodes employed large amount of binder materials to enhance the structural stability which significantly decreased gravimetric capacity of the whole electrode with limited active materials. In this work, without loss of active materials, various conducting agents were used to build electrical bridges between porous Si–C composites, which significantly improved the structural stability and hence the cycle life. Due to the increase of connection possibilities, cycle life of zero-dimensional MCMB bridged electrode reaches 80 cycles with a capacity retention of 80%, and it can be further promoted to 200 cycles for the VGCF bridged electrode and 220 cycles for the rGO bridged electrode. This work paves an effective route to construct stable Si electrode with porous structures as building blocks without the decrease of active materials.

## 1. Introduction

Silicon (Si) has presented the best candidate for the next-generation anode materials in Lithium ion (Li-ion) batteries due to its ultra-high theoretical capacity of approximately 3579 mAh/g (ca. $Li_{15}Si_4$) [1,2]. However, accompanying with the high capacity, large volume expansion during repeated electrochemical cycling results in unstable structure and hence rapid capacity fading [3,4]. Intense studies have been devoted to dealing with this volume change by reducing size of Si particles, mixing Si with inactive materials and engineering porous structures [5,6]. The ultra-high capacity of 4200 mAh/g was achieved for the first time in the Si nanowire arrays by Cui et al. which is close to the theoretical

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capacity [7]. Both theoretical and experimental works demonstrated that Si nanostructures can survive during the electrochemical process [8]. A critical size of 10 nm is good for Si nanoparticles to reach high battery performance [9]. Although various Si nanostructures including silicon nanowires, nanotubes, nanoparticles and thin film have been successfully fabricated for Li-ion battery applications, most of the nano-Si based electrodes exhibited a limited cycle life within 100 cycles [10–21]. It is found that the connection between nano-Si and conducting network cannot endure the volume expansion mismatch and thus the whole electrode still suffers from repeating structural changes even the nano-Si is still stable after cycling [22–24].

More recently, porous structures have attracted broad attention, which is considered to be one of effective approaches to solve the volume expansion problem. No matter the pores inside or surrounding active Si, they can effectively accommodate the volume expansion of Si and hence the electrodes remain unchanged after electrochemical cycling. For example, mesoporous Si, fabricated by magnesiothermic reduction of mesoporous $SiO_2$, exhibited a high capacity of 1500 mAh/g for 100 cycles [25]. Ultra-long cycle life of 2000 cycles was realized in mesoporous Si nanowires [26]. On the other hand, since the approaches for fabricating porous Si are quite limited and of high-cost, it is motivated to engineer porous Si composites which embed active Si into porous matrix. Cui et al. designed a novel Si–C composite by engineering empty space between Si nanoparticles inside carbon channels, which delivered a capacity of 800 mAh/g for 200 cycles without obvious capacity degradation [27]. The core–shell Si/carbonized PAN fibers reveal a discharge capacity of 800 mAh/g with cycle life of 300 cycles, which benefited a lot from the empties between Si nanoparticles [28]. In overall, porous Si based electrodes using above methods have exhibited quite impressive electrochemical performance [29]. However, the unique structural configurations in these works compared to the conventional Li-ion batteries are not suitable for practical battery applications due to the complex synthetic process and extremely low yield. Focusing on this point, much effort has been made to fabricate and assemble Si based anode in conventional way. Porous Si–C composites, fabricated by a facile spray drying method which generated numerous pores inside by sacrificing $SiO_2$ nanoparticles, can deliver a discharge capacity of 1400 mAh/g with a cycle life of more than 150 [30]. The significant achievement in these porous Si–C composites seems to raise the light for obtaining stable Si anodes with long cycle life in a facile and universal manufacturing approach. However, after careful review, it is found that most of the porous Si based electrodes in conventional configuration rely on the use of large amount of conducting agents and binder materials. As a result, the content of active materials in these electrodes was greatly reduced to less than 60% which is obviously lower than normally accepted value of above 80%. For example, only 40 wt% of the electrode is the active material in the interweaved Si@SiOx/C nanoporous spheres anode [31]. The 60 wt% active materials were widely used in no matter mesoporous Si or porous Si–C composites etc. [25,30,32,33]. Thus, understanding of what happened in the porous Si based electrodes and how to remain the high battery performance without decreasing content of active materials plays the significantly important role in the use of porous Si–C electrodes for practical battery applications.

Herein, porous Si–C composites were fabricated through a facile spray-drying and post-etching method, as shown in Fig. 1a. It was found that the large surface area in porous Si–C composites leaded to the absorption of binder materials and hence low adhesion strength in the electrode. In order to improve structural stability and also electrochemical stability without sacrifice of active materials, various conducting agents were used to bridge the porous Si–C composites, including zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) systems, as illustrated in Fig. 1b. Systematical studies demonstrated that the effective electrical connections among Si–C composites could significantly promote the electrochemical performance. Discharge capacity of 800 mAh/g can be retained for 200 cycles in vapor-grown carbon fiber (VGCF) and reduced graphene oxide (rGO) bridged electrodes.

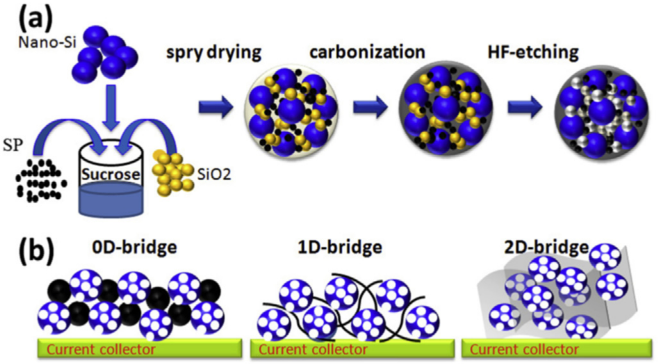

**Fig. 1.** Schematic of the fabrication of a) porous Si–C composite and b) conducting agents bridged electrodes.

## 2. Experimental

### 2.1. Preparation of porous Si–C composites and corresponding electrodes

Fig. 1a presents the typical fabrication process of porous Si–C composites. Si powders (Sinopharm Chemical Reagent Co., Ltd, 81012160) were used as the raw materials without any further treatment. By milling the Si powders for 12 h in a high-speed ball-milling machine, Si nanoparticle slurry was obtained. Subsequently, $SiO_2$ nanoparticles (Taijihuan Co., Ltd, $SiO_2$-1), sucrose (Sinopharm Chemical Reagent Co., Ltd, 10021418) and super-P (SP) (Shanghai hui industrial chemical co., LTD) were added into the Si nanoparticles slurry with a weight ratio of Si: $SiO_2$: sucrose: SP = 10:10:30:1. After spray drying of the as-prepared mixture, powders were heated at 900 °C for 5 h with continuous Ar flow. Then, porous Si–C composites were obtained by a HF treatment and subsequent washing with deionized (DI) water three times.

As shown in Fig. 1b, various porous Si–C electrodes were fabricated by mixing active materials (porous Si–C composites, 80 wt%), binder materials (sodium alginate, 10 wt%) and conducting materials (10 wt%). The original porous Si–C electrode employs the broadly used SP as conducting materials. In other modified porous Si–C electrodes, a part of SP (4 wt% or 2 wt% of the electrode) was replaced by other conducting materials to bridge the Si–C composites, including MCMB (Tianjin BET, new energy materials co., LTD), VGCF (Showa Denko, VGCF-H), carbon nanotubes (CNTs) and rGO. CNTs used in this work with a length of 100 μm and diameter of 15–20 nm were prepared from the decomposition of cyclohexane by in situ formed Fe nanoparticles from ferrocene in a chemical vapor deposition process. rGO was prepared by annealing graphene oxide (GO) at 900 °C in Ar atmosphere and GO was synthesized from natural graphite flakes using a modified Hummers method as reported in our previous work [34]. Finally, the electrodes were obtained by casting and drying above slurry onto a cooper foil and then pressing at a high pressure of 4 Mpa.

### 2.2. Structural and electrochemical characterizations

The surface morphology of porous Si–C composites was