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Porous Silicon–Carbon Composite Materials Engineered by Simultaneous Alkaline Etching for High-Capacity Lithium Storage Anodes

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ABSTRACT

Porous silicon–carbon (Si–C) composite materials have attracted a great deal of attention as high-performance anode materials for Li-ion batteries (LIBs), but their use suffers from the complex and limited synthetic routes for their preparation. Herein we demonstrate a scalable and nontoxic method to synthesize porous Si–C composite materials by means of simultaneous chemical etching of Si and carbon phases using alkaline solution. The resulting porous Si–C composite material showed greatly improved cycle performance, good rate capability, and high dimensional stability during cycling. Porous Si–C electrode showed an expansion of the height by about 22% after the first lithiation and only 16% after the first cycle. The material synthesis concept and scalable simultaneous etching approach presented here represent a means of improving the electrochemical properties of Si-based porous anode materials for use in commercial LIBs.

1. Introduction

Lithium-ion batteries (LIBs) have played important role in the development of portable electronics and have also gained a great deal of attention as power sources for emerging applications such as electric vehicles and large-scale energy storage systems [1–3]. However, in order to meet recent requirements for aforementioned emerging applications, the electrochemical performance of LIBs needs to be further advanced in terms of energy density and power density [4–6]. In an attempt to increase the energy density of LIBs, development of new electrode materials with higher capacity than currently used materials such as $LiCoO_2$ and graphite has been pursued during the past several decades [7–9].

Silicon has been regarded as a particularly promising candidate anode material to replace graphite, because its capacity (3579 mAh g^{-1}) is about ten times higher than that of graphite (372 mAh g^{-1}) [10,11]. However, the practical use of Si has been limited by its extremely large volume changes during alloying and dealloying reactions with Li, leading to poor capacity retention of Si electrodes [12–14]. Various strategies have been suggested to solve these problems of Si anodes, and some of them showed improved capacity retention by managing the volume changes of Si during cycling [15]. Among these promising Si-based anode materials, Si–C composites are being regarded as highly promising anode materials because of their stable cycle performance and relatively low production cost [16–19]. Porous Si-based materials have also showed some promising behaviors, because pores in the material could effectively accommodate the mechanical strain induced by alloying and dealloying reactions of Si with Li, thereby minimizing mechanical degradation of the resulting Si-based electrodes. In this regard, many approaches to prepare porous Si-based materials have been investigated, and some examples of porous Si-based materials showed good cycle performance comparable to that of currently used graphite anode materials for LIBs [20–22]. However, most of the approaches to prepare porous Si-based anode materials require either time-consuming and expensive processing or the use of hazardous chemicals such as hydrofluoric acid and silane gas, making production process expensive [23,24]. Given that the production cost of LIBs is one of the most challenging issues for their successful use in emerging applications for electric vehicles and large-scale energy storage systems [25], further addressing this technical issues of porous Si-based anode materials is necessary to ensure their commercial success.

Toward a scalable and cost-effective process to produce porous Si-based anode materials, here we demonstrate a facile route for the preparation of porous Si–C composites by means of simple ball milling followed by simultaneous one-pot chemical etching of Si

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and carbon phases in the Si–C composite using alkaline (NaOH) aqueous solution. By using this method in the present work, we could obtain porous Si–C composites with the pores inside the composite as well as at the surface of the composite, because alkaline solution has the capability to etch both carbonaceous materials and Si [26–30]. Pan et al. synthesized a york–shell Si–C nanocomposite by forming a void between the Si nanoparticle and the carbon shell using NaOH etching of the Si nanoparticle [31]. Instead of embedding Si particles in hollow carbon shell, it has been recently revealed that the structure of porous carbon surrounding nanoscale Si can accommodate the large volume changes of Si during lithiation and delithiation, thus showing outstanding cycle performance [32,33]. However, the methods used thus far to generate pores in the carbon phase are complicated or involve toxic chemicals. Considering that both ball milling and alkaline etching are environmentally benign and already established in the industrial processes, our simple alkaline etching combined with ball-milling process would be another promising synthetic routes for porous Si–C composite anode materials for next-generation LIBs. In this work, we describe this method in detail and demonstrate its promise for the preparation of porous Si–C composite anode materials for use in next-generation LIBs.

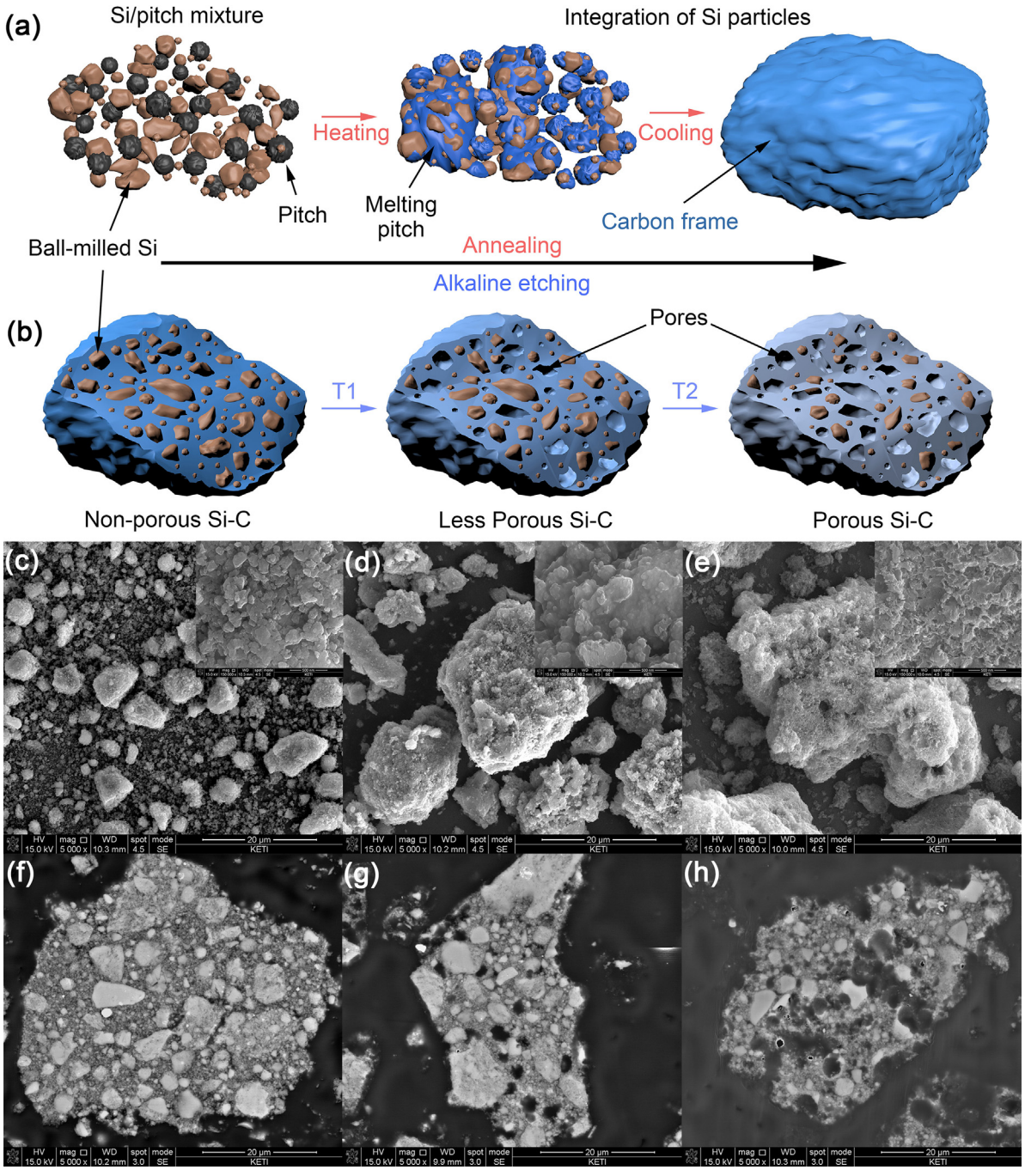

Fig. 1. Schematic illustration of synthesizing (a) non-porous Si–C composite through annealing (heating and cooling) and (b) porous Si–C composite by etching non-porous Si–C in alkaline solution for times of T1 (105 min) and T1 + T2 (115 min). Powder SEM images of (c) ball-milled Si, (d) non-porous Si–C, and (e) porous Si–C composite (T1 + T2). Cross-sectional SEM images of (f) non-porous Si–C, (g) less porous Si–C (T1), and (h) porous Si–C (T1 + T2).