The Preparation and Electrochemical Performance Analysis of Different Porous Silicon Composites

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Abstract

In this work, porous silicon is prepared via one-step LiAlH₄ reduction method, and then nano-silver(AgNPs) and Li₂CO₃ are attached to porous silicon substrate to form different porous silicon composites. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are applied to characterize the morphology of porous silicon composites, and porous silicon composites are tested via electrochemical techniques. The experimental results present that porous silicon composites loaded with AgNPs (Si-Ag) show higher specific capacity (476.0195 mA·h·g⁻¹) with the two obvious reduction potential of ~0.3 V and ~0.1 V, and lower interfacial impedance (~0.8 Ω) in those composites material. Si-Ag composites are suitable to be used as anode materials for lithium-ion batteries.

Keywords

Porous silicon · Porous silicon composites · AgNPs · Lithium-ion battery

1 Introduction

Lithium-ion batteries have the advantages of high temperature, high capacity and low voltage of traditional batteries, and also possess the merits of long service life and excellent performance, which endow lithium-ion batteries wide applications such as mobile electronic equipment, new energy vehicles, space technology and defense industry [1, 2]. Recently, lots of novel lithium-ion batteries are being developed with the in-depth study of battery composite materials [3, 4]. Anode materials still occupies a large market proportion in main material of the lithium-ion battery. At present, graphite is the most widely used anode material in lithium-ion battery, but the theoretical specific capacity (372 mAh/g) of it is low, which will limit energy storage and fail to meet the increasing demand for high energy of products. Therefore, it is necessary to develop a novel anode material.

Silicon-based materials have become the research focus of anode materials for lithium-ion batteries due to the advantages of high theoretical specific capacity (4200 mAh/g), low charging and discharging platform, easy modification of nanostructures and the ability to form metal silicide with many metal elements [5–8]. Silicon-based composite material shows a superior performance and application prospect, especially the alloying of cathode material such as silver nanoparticles in lithium-ion battery which not only endows lithium-ion battery the high conductivity, also overcomes the problem of silicon volume expansion in the process of charging and discharging [9–13]. The electrochemical properties of lithium-ion battery are greatly improved via silicon-based anode materials.

Inspired by previous studies, the generation of porous silicon was based on the reduction of LiAlH₄ which served as a substrate of nano-silver (AgNPs) and Li₂CO₃ to prepare the porous silicon composites (Si-Ag, Si-Li₂CO₃ and Si-Ag-Li₂CO₃) in this paper. The morphology of porous silicon composite materials was characterized by SEM and XRD, and the electrochemical performance was also tested which provided experimental basis for the development of lithium-ion battery based on silicon anode materials.
2 Experimental

2.1 The Preparation and Testing of Battery

First, the mixture of different porous silicon composites, acetylene black and teflon (m₁:m₂:m₃=80:15:5) were prepared with ethanol, and it was sonicated for 30 min. Subsequently, the mixture was heated at 80°C until it became sticky. The mixture was smeared to battery pole piece, and then the porous silicon composites-modified pole piece was kept at 80°C for 10 h following by tableting. The prepared battery pole piece was immersed into 6 M KOH for 18 h in order to test the electrochemical property in 6 M KOH.

The details of materials and reagents and apparatus was in Supporting Information, and the preparation process of porous silicon, AgNPs and silicon composites was also in Supporting Information.

3 Results and Discussion

3.1 The Principle of Preparation of Porous Silicon

The structure of porous silicon is the prerequisite for performance of porous silicon composites. In this work, LiAlH₄ was used to reduce white carbon black at high temperature according to Eq. (1):

\[ \text{LiAlH}_4 + \text{SiO}_2 \rightarrow \text{LiAlO}_2 + \text{Si} + 2\text{H}_2 \]

Absolute dry conditions are necessary during the reaction due to the nature of water explosion of LiAlH₄.

3.2 The Characterization of Porous Silicon Composites

XRD was employed to verify the composition and crystal structure of different porous silicon composites. In the XRD spectrum of Si-Ag composites (Fig. 1A), the main diffraction peaks of Si-Ag composites were observed at 38.083° (111), 44.527° (200), 64.291° (220) and 77.426° (311) which corresponded to Ag (JCPDS no. 04-0783); 48.38° (220), 52.75° (311) and 81.56° (222) were the characteristic peaks of the standard Si (JCPDS no. 35-1158). This result showed the successful attachment of AgNPs to porous silicon [14, 15]. Figure 1B showed XRD spectrum of Si-Li₂CO₃ composite. The diffraction peaks (48.38° (220) and 52.75° (311)) were assigned to standard Si (JCPDS no. 35-1158), and other peaks were corresponded to standard Li₂CO₃ diffraction peak (JCPDS no. 22-1141). However, the diffraction peak of Si was weak, which might be due to the structure of porous silicon. As shown in Fig. 1C, the diffraction peaks of standard Ag (JCPDS no. 04-0783) and standard Li₂CO₃ (JCPDS no. 22-1141) were all observed. This result indicated the successful attachment of AgNPs, Li₂CO₃ and porous silicon. All of those results suggested the successful preparation of porous silicon composites.

SEM was applied to characterize the morphology of porous silicon composites. As shown in Fig. 2A, some pores were presented in porous silicon with a pore size of about 10-15 μm, but the pores were destroyed and incomplete. It might be due to the high calcination temperature which was harmful to the formation of internal porous structure. Some attachments were observed in the insert of Fig. 2A which was possibly carbon residue. The pore structure in Si-Ag porous silicon was very obvious in the insert of Fig. 2B, and some attachments were seen which might be AgNPs and carbon residue (Fig. 2B). Likewise, Fig. 2C showed that the pore structure was seriously damaged at a; and Li₂CO₃ and carbon residue were unevenly distributed on the surface of porous silicon in the insert of Fig. 2C. As could be seen from Fig. 2D, only a few porous structures of porous silicon were be destroyed; and solid particles of different shapes were observed in the insert of Fig. 2D), which might be carbon residue, Li₂CO₃ and AgNPs.

Subsequently, TEM was also applied to depict the morphology of those porous silicon composites. As shown in Fig S1A, the crystal structure of porous silicon was observed. In the TEM images of Si-Ag and Si-Li₂CO₃ porous composites (C)
silicon composites (Fig S1B, C), AgNPs and Li$_2$CO$_3$ were evenly distributed in the pore of porous silicon, respectively. The lattice of porous silicon was not observed in Si-Ag-Li$_2$CO$_3$ composites, which was because the thick coating layer covered the lattice of porous silicon (Fig. S1D). Those results suggested the successfully preparation of those porous silicon composites.

3.3 The Electrochemistry Testing of Porous Silicon Composites

CV was applied to investigate the electrochemical behavior of these porous silicon composites in 6 M KOH at a scan rate of 0.1 V·s$^{-1}$, and the potential was from -1 V to 1 V. As shown in the cyclic voltammogram of Si-Ag (Fig. 3A), a weakly oxidation peak was observed at the potential of ~0.2 V while an oxidation peak also was seen at the potential of ~0.5 V, which was ascribed as the oxidation process of AgNPs to Ag$_2$O and Ag$_2$O to AgO. Two obvious reduction peaks were seen at the potential of ~0.3 V and ~0.1 V, which was due to the reduction of AgO to Ag$_2$O and Ag$_2$O to AgNPs. In the cyclic voltammogram of Si-Li$_2$CO$_3$ (Fig. 3B), the oxidation current appeared and the curve began to rise at the potential of 0.25 V, indicating the extraction of Li$^+$ from porous silicon composites. An obvious reduction peak appeared at the potential of ~0.3 V which corresponded to the alloying process of Li$^+$, indicating the activation of electrode active substance. An indistinct oxidation peak was seen at the potential of ~0.2 V, which was due to the formation of solid electrolyte interface (SEI) film between electrolyte and electrode active substance [16]. In the cyclic voltammogram of Si-Ag-Li$_2$CO$_3$ (Fig. 3C), at about 0.25 V and the current began to rise, indicating that ions of Ag$^+$ and Li$^+$ had begun to extract; and a very obvious reduction peak appeared at ~-0.16 V, which might be due to the insertion of Ag$^+$ which leaded to alloying of silicon.

The specific capacitance ($C$) of these porous silicon composites was estimated according to Eq. (2):

$$C = \frac{S}{2(v \times s \times m)}$$

where $S$ is the integral area of the cyclic voltammogram, $v$ is the potential and $m$ is the mass of material [17, 18]. The specific capacitance of these porous silicon composites was calculated in Table 1, and the comparison of specific capacitance of different materials was also listed in Table 1. As shown in Table 1, the specific capacitance of Si-Ag porous silicon composites was higher than that of other materials.
silicon composites was higher than many of others materials, indicating that Si-Ag porous silicon composites possessed satisfied electrochemical performance.

EIS was used to further explore the electrochemical characteristics of porous silicon composites. The open circuit voltage was maintained at about 1.3 V. The test frequency of EIS was 0.01~100 kHz, and the amplitude was 0.005 V. In Nyquist plot, the diameter of semicircle represented the charge transfer resistance (Rct) between solution and electrode surface [21]. As shown in Fig. 4, The Rct of Si-Ag, Si-Li2CO3 and Si-Ag-Li2CO3 porous silicon composites was respectively ~0.78 Ω, ~0.8 Ω and ~1.4 Ω. The Rct of Si-Ag-Li2CO3 composites was larger than that of Si-Ag composites, which might be the generation of SEI film. SEI made ions pass through successfully, but electrons could not pass through it [22]. On the one hand, the formation of SEI increased the interface resistance of electrode and electrolyte. Therefore, Si-Ag composites possessed better electrochemical performance.

### 4 Conclusions

In a word, porous silicon-based composite materials showed good electrochemical performance, and the prepared process of porous silicon via one-step LiAlH4 reduction method was simple and cost effective. Among those composite materials, Si-Ag composites have higher specific capacity and lower interface impedance, which presented the best electrochemical performance. This method for preparing electrode materials possessed the advantages of simple operation, low cost and environment friendly, which gave those materials the application potential in industry.
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Data Availability  All data during this study are included in this manuscript.

Declarations

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Research Involving Human Participants and/or Animals  Not applicable.

Consent for Publication  All of co-authors have agreed to publish this manuscript.

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