

## Review

## High performance germanium-based anode materials



Zhenglin Hu, Shu Zhang, Chuanjian Zhang, Guanglei Cui\*

Qingdao Industrial Energy Storage Technology Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

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## ABSTRACT

Germanium has attracted much attention in recent decades due its intrinsic suitability for use in lithium-ion batteries. It has a high capacity ( $1384 \text{ mA h g}^{-1}$ , corresponding to  $\text{Li}_{15}\text{Ge}_4$ ), excellent lithium-ion diffusivity (400 times faster than Si), and high electrical conductivity ( $10^4$  times higher than Si). However, its range of applications is hindered by the huge volume change during the lithiation and delithiation process ( $\sim 250\%$  in a lithiated state for  $\text{Li}_{15}\text{Ge}_4$  and  $\sim 300\%$  for  $\text{Li}_{22}\text{Ge}_5$ ), thereby resulting in electrode pulverization and its isolation from the current collector, which finally leads to the loss of capacity and poor cycling performance. Much research has been conducted to improve the electrochemical performance of germanium materials with great success in recent years. The present review focuses on the synthetic routes and novel electrode structures used for germanium anodes to obtain electrodes with excellent performance. To present these experimental results in a systematic manner, they are categorized as follows: (i) nanostructured germanium; (ii) porous anode materials; (iii) coating or doping designs; (iv) alloyed germanium materials; (v)  $\text{GeO}_2$ -based anode materials; and (vi) the future outlook is considered. Finally, our personal perspectives on germanium electrode design are presented as well as suggestions for further research into novel germanium anode materials.

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\* Corresponding author.

E-mail address: [cuiql@qibebt.ac.cn](mailto:cuiql@qibebt.ac.cn) (G. Cui).

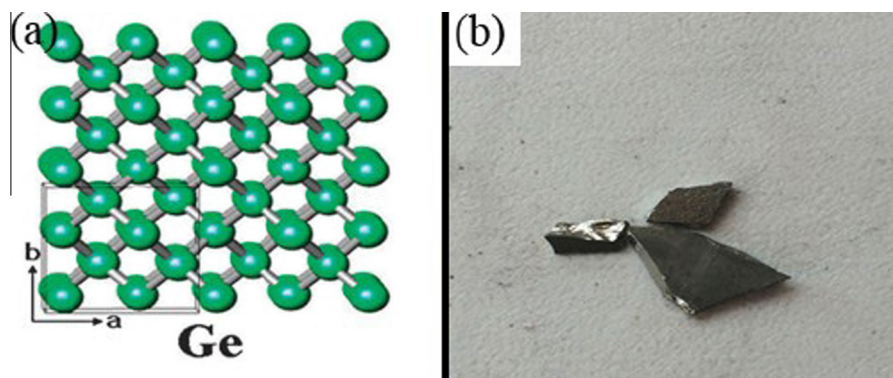


Fig. 1. Crystalline structure (a) and photograph (b) of a germanium crystal. Reproduced with permission [3]. Copyright 2010 Royal Society of Chemistry.

## 1. Introduction

Due to the decline in finite fossil fuel reserves and severe pollution, researchers around the world are trying to develop novel substitutes. Lithium-ion batteries (LIBs) are promising rechargeable storage devices, which have many advantages, particularly because they are environmentally friendly and renewable. Most commercially available LIBs contain graphite-based anode materials with a theoretical storage capacity of  $372 \text{ mA h g}^{-1}$  ( $837 \text{ mA h cm}^{-3}$ ) [1], which corresponds to the lithiated state of  $\text{LiC}_6$ . However, graphite-based materials have a low storage capacity, so they can never meet the increasing social demand for high-performance energy storage for equipment such as portable electronic devices, electric vehicles, and implantable medical devices [2]. Group IV elements such as tin (Sn), silicon (Si) [3], and germanium (Ge) [4,5] are all regarded as promising alternative candidates due their high storage capacities for application in LIBs.

Germanium (Ge) was discovered by Clemens A. Winkler at Freiberg, Germany in 1886. The atomic weight of germanium is 72.64 with a density of  $\sim 5.5 \text{ g cm}^{-3}$ . Germanium is categorized as a metalloid element in group IVA and it has five naturally occurring isotopes. The physical and chemical properties of germanium are very similar to those of silicon and its unit cell structure is depicted in Fig. 1(a) [3]. In this condition, germanium is a face centered cubic crystal ( $\alpha$ -germanium) and its lattice parameters are:  $a = b = c = 565.75 \text{ pm}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . Germanium is grayish-white, lustrous, and possesses similar chemical properties to Sn and Si under standard conditions. Germanium is also brittle, as shown in Fig. 1(b), and it is one of the few substances to exhibit an increase in volume when it solidifies, in the same manner as water. The pure germanium element can be doped with arsenic or other elements and used as a transistor in electronic applications [6]. Germanium is non-toxic and it is used widely in solar cells, polymerization catalysts, phosphors, metallurgy, and chemotherapy [7,8].

It should be noted that silicon has been investigated widely due to its intrinsic electrochemical properties, such as its low voltage profile and high theoretical capacity ( $3590 \text{ mA h g}^{-1}$  for the  $\text{Li}_{15}\text{Si}_4$  phase at room temperature), which is about 10 times that of carbonaceous materials (about  $372 \text{ mA h g}^{-1}$ ) [9]. Silicon is an abun-

dant element in the earth's crust so its cost is relatively low. However, there are several challenges when using silicon as the anode in LIBs, including its intrinsic poor electrical conductivity, huge volume change ( $\sim 300\%$ ), and the instability of the solid electrolyte interface (SEI) layer [10,11], which contribute to the destruction of the electrode's structure and the loss of storage capacity. The lithium ion diffusion rate and high electrical conductivity of germanium are better than those of silicon, so it is highly suitable as an anode material for LIBs despite its high cost. Germanium can react with lithium to form Li-Ge alloys during the lithiation process [12]. Therefore, germanium-based materials undergo severe volume expansion ( $\sim 250\%$  for  $\text{Li}_{15}\text{Ge}_4$ ) [13] and contraction during the lithiation/delithiation process, which contribute to the structural failure of electrode materials and various side reactions. Therefore, significant efforts have been made to address these issues. Various novel electrode materials have been designed such as nanostructured germanium electrodes, germanium-based composite electrodes, and alloy electrodes.

This review starts by providing an overall analysis of the advantages of germanium compared with silicon and the intrinsic defects of germanium as an anode material for LIBs, before describing several strategies for capacity enhancement. These strategies are categorized as follows: i) nanostructured germanium, including nanoparticles (NPs), nanowires (NWs), and nanotubes (NTs); ii) porous anode materials; iii) coating or doping designs, including Ge/C composites, core-shell nanocomposites, and other designs; iv) alloyed germanium anodes, including binary alloys such as Ge/Sn, Ge/S, Ge/Se, and Ge/N, and ternary alloys such as  $\text{CuGeO}_3$ ,  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ ,  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Co}_2\text{GeO}_4$ ,  $\text{Cd}_2\text{GeO}_4$ ,  $\text{PbGeO}_3$ ,  $\text{SrGe}_4\text{O}_9$ , and  $\text{BaGe}_4\text{O}_9$ ; v)  $\text{GeO}_2$ -based anode materials. Finally, a summary is provided as well as an overview of the outlook for the application of germanium in sodium ion batteries (SIBs) in order to give deeper insights into germanium anode materials.

## 2. Advantages of germanium over silicon

Due to modern social development, traditional carbonaceous electrode materials cannot meet the growth in demand and thus high performance electrode materials are urgently required. The

Table 1

Comparison of the theoretical specific capacity, charge density, and volume change for various anode materials.

Materials	Li	C	Si	Ge	Sn	Sb	Al	Mg	Bi
Density ( $\text{g cm}^{-3}$ )	0.53	2.25	2.33	5.35	7.29	6.7	2.7	1.3	9.78
Lithiated phase	Li	$\text{LiC}_6$	$\text{Li}_{4.4}\text{Si}$	$\text{Li}_{15}\text{Ge}_4$	$\text{Li}_{4.4}\text{Sn}$	$\text{Li}_3\text{Sb}$	LiAl	$\text{Li}_3\text{Mg}$	$\text{Li}_3\text{Bi}$
Theoretical specific capacity ( $\text{mAh g}^{-1}$ )	3862	372	4200	1384	994	660	993	3350	385
Volume change (%)	100	12	320	230	260	200	96	100	215

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