



# Electrodeposited Germanium/Carbon Composite as an Anode Material for Lithium Ion Batteries



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## ABSTRACT

We demonstrate the synthesis of nano Ge/C composite using a facile and cost-effective electrochemical deposition method, and its application as an anode material in Li-ion batteries. Nano Ge/C composite is electrodeposited directly on Cu foil in ethylene glycol containing  $\text{GeCl}_4$  and carbon black. The Ge particles with an average size of  $\sim 20$  nm are uniformly covered with carbon. Compared with the pure Ge electrode, the Ge/C electrode exhibits a higher first reversible capacity of  $1224 \text{ mA g}^{-1}$ , and maintains a capacity of  $1095 \text{ mAh g}^{-1}$  at  $0.1\text{C}$  over 50 cycles. Even at the high rate of  $2\text{C}$ , the capacity of the Ge/C electrode is still high at  $972 \text{ mAh g}^{-1}$ . The presence of carbon black and pores in the Ge/C electrode improves the conductivity of the electrode, and mitigates the stress inside the electrode by supplying buffer volume, leading to the enhanced electrochemical characteristics of the electrode. Further, the full Li-ion cell composed of Ge/C anode and  $\text{LiCoO}_2$  cathode exhibits good cyclability, rate capability, and coulombic efficiency.

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## 1. Introduction

Li-ion batteries (LIBs) have been widely used in portable electronic devices such as the cellular phone, laptop, and digital camera. Moreover, the increasing demand for electric vehicles (EVs) and hybrid electric vehicles (HEVs) is for batteries of high-energy density, light weight, and small volume [1–4]. However, the current LIBs using  $\text{LiCoO}_2$  as a cathode material and graphite as an anode material cannot meet the industry's energy requirements, especially for longer driving distances by battery for EVs, due to material limitations [5–7]. From this aspect, increasing the specific capacity of the anode in LIB is considered a potential route to increase the energy density of batteries.

Graphite has been used since 1994 as a commercial anode material for Li-ion batteries. However, it has the limited theoretical capacity of  $372 \text{ mAh g}^{-1}$ , which is not considered sufficient for modern batteries. Thus, much research has focused on developing alternative materials with higher specific capacity than graphite [7–13]. Li alloy based anode materials, such as Si ( $4200 \text{ mAh g}^{-1}$ ), Ge ( $1620 \text{ mAh g}^{-1}$ ), and Sn ( $990 \text{ mAh g}^{-1}$ ), have higher Li storage

capacity compared with graphite, and are expected to replace graphite in LIBs [7,12,14–16]. Among the materials, germanium (Ge) has attracted attention, due to its high specific capacity, high electrical conductivity, high ionic conductivity, and low lithiation potential [17–21]. Although Ge has lower theoretical capacity and it is somewhat less economical compared with Si, it exhibits some attractive superior properties to Si [22,23]. The lower band gap of Ge enables  $10^4$  times higher conductivity of Ge compared with that of Si. Moreover, the room-temperature diffusivity of Li in bulk Ge is 400 times higher than that of Si. These superior properties of Ge make it a more preferable anode material to Si [23–25].

Despite these promising characteristics, pure Ge electrode suffers from poor cycle life due to severe mechanical cracking and pulverization by significant volume change occurring during lithiation/delithiation [26–28]. To address this problem, various attempts have been made, such as decreasing the active material's particle size [19,29], dispersing the active material into an inorganic inactive/active buffer matrix [27,28,30,31], using amorphous active materials [32,33], and forming composites with conductive carbon buffer [34–37]. Among these, to make composites with carbon has been considered most attractive, due to the excellent electrochemical characteristics of the composites and light weight of carbon [38]. In particular, Forney et al. reported that the composite of Ge with carbon nanotube

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(CNT) could deliver capacity as high as  $12 \text{ mAh cm}^{-2}$ . This value is much higher compared with that of commercial LIBs, in which the specific capacity of anode is controlled about  $2 \text{ mAh cm}^{-2}$  [39]. In another work, Dileo et al. reported the superior electrochemical performance of hybrid Ge-nanoparticles (NPs)- single wall CNT such as high initial coulombic efficiency, good cyclability, and high specific capacity [40]. Nevertheless, the preparation of the Ge-NPs by injection chemical vapor deposition (CVD) process requires sophisticated systems. Moreover, this method is favorable on lab-scale production.

Electrodeposition has been considered as a simple, economical, and mass-scalable method to fabricate metallic coating for decorative or corrosion resistant purpose. Further, this technique is also applicable to fabricate a thin layer of high-quality Ge on a conductive surface [40,41]. In particular, the fabrication of Ge thin film by electrodeposition is much more economical compared with other deposition methods using vacuum process. In this study, we made a composite of Ge/C from a carbon dispersed electrolytic bath by electrodeposition. Through the electrodeposition, Ge could be directly deposited on the Cu substrate, in which Ge active materials could make a better binding with Cu substrate, compared with the case using binder. Furthermore, the loading mass on the resulting electrode due to the synthesis of freestanding sample without using binder and conductive additive is higher compared to the samples prepared by slurry method. This can lead to a higher specific capacity of electrode when calculated based on the total mass of electrode.

In this study, we proposed a simple method to fabricate the composite thin film of Ge and carbon (Ge/C) by electrodeposition method. This deposited film was directly used as an anode, in which additional binders and conductive additives were not necessary, for Li-ion battery. In particular, we compared the electrodeposited composite film of Ge/C with the electrodeposited pure Ge in aspects of specific capacity, cyclability, and rate capability. Further, we investigated the applicability of the prepared electrodeposited Ge/C anode in Li-ion battery by combining it with a  $\text{LiCoO}_2$  cathode.

## 2. Experimental

### 2.1. Material synthesis

The Ge/C composite film was fabricated using an electrodeposition method. In particular, 10 mg carbon black was added to

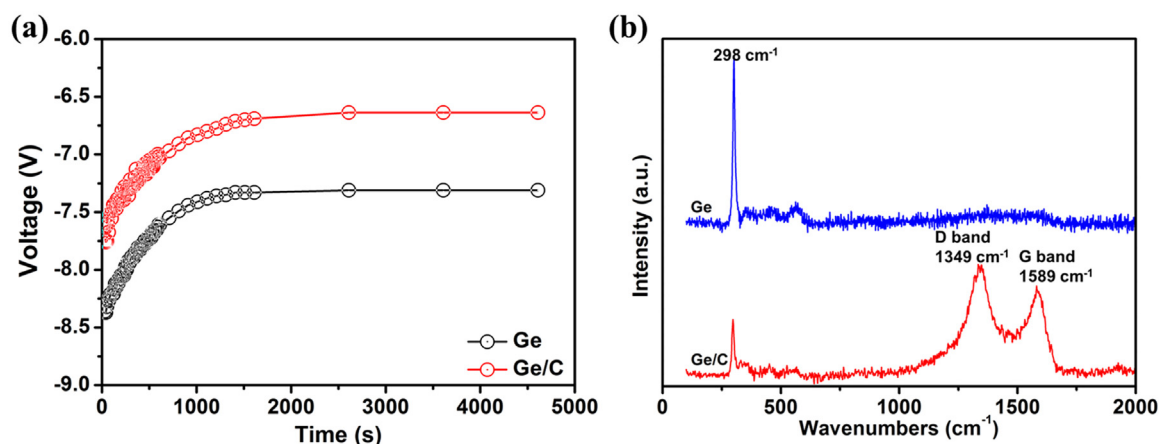
48.5 ml ethylene glycol (Sigma-Aldrich 99.8%), and the mixture was ultrasonically stirred for 3 h to make a homogeneous suspension. The obtained homogeneous suspension was then transferred to glove box and 1.5 ml  $\text{GeCl}_4$  was injected into the suspension with stirring. The Ge/C composite was galvanostatically electrodeposited on a  $2 \times 2 \text{ cm}^2$  Cu foil at room temperature under the optimized current density of  $80 \text{ mA cm}^{-2}$  using a three-electrode system. For comparison, pure Ge thin film was also electrodeposited on the Cu foil in the same condition, except for the addition of carbon. It should be noted that, before the electrodeposition, the Cu foil was pickled in 10% HCl to remove the native surface oxide, followed by washing with acetone, and drying in vacuum. The graphite plate and saturated calomel electrode were used as a counter electrode and reference electrode, respectively. The electrodeposited Ge and Ge/C samples were sequentially rinsed with methanol several times, and dried in vacuum at  $70^\circ\text{C}$ . The samples were then stored in glove box, before further electrochemical tests.

### 2.2. Physical characterisation

We observed the morphology of the Ge and Ge/C electrodeposits using field emission scanning electron microscopy (FE-SEM; S-4700/EX-200), and transmission electron microscopy (TEM; TECNAL-G<sup>2</sup>). We also used the attached energy dispersive X-ray spectroscopy (EDS) to analyze the composition of the Ge/C electrodeposit. A Raman spectrometer (JYHR-800, HORIBA JOBIN YVON) using an excitation laser beam with a wavelength of 514 nm was employed to analyze the structure feature of outcome. The carbon content in Ge/C sample was further determined by CHNS elemental analysis (EA-1110, CE Instruments).

### 2.3. Electrochemical characterisation

To investigate the electrochemical characteristics of Ge/C composite and pure Ge, the samples were punched into 14 mm diameter disks. The disk electrodes were assembled in Ar-filled glove box with a Li metal foil counter electrode and a glass fiber separator impregnated with an electrolyte of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, by vol%) in the 2032 coin-type half cells. The loading-mass of Ge/C or Ge on electrodes was controlled to around  $1 \text{ mg cm}^{-2}$ . We investigated the electrochemical characteristics of Ge/C and Ge by cyclic voltammetry (CV) in the potential range of 0 ~ 3 V vs.  $\text{Li/Li}^+$  using a



**Fig. 1.** (a) Potential variation during the electrodeposition of Ge and Ge/C at the applied current density of  $80 \text{ mA cm}^{-2}$ , respectively. (b) Raman spectrum for the Ge and Ge/C, respectively.

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