In the germanium–carbon nanotubes–copper monolith anode, the carbon nanotube (CNT) network enhances the electron migration in the electrode and the elastic matrix buffers the volume expansion of Ge active particles. The improved rate and cycling performance endow this elastic monolith as an attractive candidate for lithium batteries’ anode.

Today’s consumer electronics markets, especially Electric Vehicles (EVs) and smart grids, call for lithium-ion batteries (LIBs) with a superior energy density, as well as a long cycle life. Natural graphite has dominated the LIBs markets for years because of its stable cycling performance during the lithiation and delithiation processes and its abundant reservoir. However, the theoretical gravimetric and volumetric capacities of graphite are restricted to 372 mA h g\(^{-1}\) and 837 mA h cm\(^{-3}\), respectively, which limit its further application in high energy density LIBs. For this reason, various anode materials with an advanced capacity ability have been investigated as an alternative.

Group IVA elements (Si, Ge, Sn), which can be alloyed with lithium, are considered as fantastic alternative anode materials for graphite because of their relatively high theoretical capacities (at least 3 times higher than graphite). Unfortunately, a tremendous volume change will inevitably occur during the charge and discharge processes, which leads to material pulverization and finally to the material being electrically isolated from the current collector. As a result, capacity fading and poor cycling performance are always observed when using this kind of material. Hence, it is still a huge challenge to realize a stable energy delivery for commercial application of an alloy anode in LIBs. Several efforts have been devoted to overcome the problems above. Downsizing the active particle to the nanometer scale, which could reduce the absolute volume change in a single particle, is believed to be one of the efficient routes to realize an improved cycle life. For this reason, nanowires\(^{5,6}\), nanotubes,\(^{26,36}\) and nanoporoporous structures\(^{40,57}\) have been successfully employed as alloy anodes, which exhibit an enhanced cycling performance. The other powerful strategy is introducing a buffer phase, which could be electrochemically active or inactive, to construct a composite electrode. A typical example of the application of an inactive matrix is a silicon composite with its oxide. At the same time, the use of carbonaceous materials, as both structure cushions and conductive additives, has been widely adopted to improve the electrochemical performances of alloy anodes. Carbon nanotubes (CNTs)\(^{9}\) and Graphene\(^{10}\) have always been chosen as an important component for alloy–carbon composite anodes due to their outstanding electrical properties and unique 1D/2D structure, respectively. Additionally, dispersing active nanoparticles in a carbon matrix could also relieve the stress originating from the volume expansion, so as to optimize the cycle life of batteries, and this has been demonstrated in the literatures.\(^{7,11}\) Because of the use of high capacity alloy anodes, all the approaches employed above have increased the energy density to some extent.

However, conventional electrode fabrication methods mix active materials with polymer binders and conductive additives to form a thin film on the current collector. This definitely leads to a significant decrease in energy density. Meanwhile, due to the presence of inert binders and additives, the Li ion migration rate of the electrode also declined significantly, which resulted in a poor rate capability.\(^{12}\) Hence, well-designed three-dimensional (3D) electrodes with nanostructured architectures, which are favorable for both a fast electron transfer and an enhanced energy density, have attracted a great deal of attention.\(^{13}\)

In this paper, a well-designed 3D germanium–carbon nanotubes–copper foam monolith as an anode for rechargeable lithium batteries was constructed without any polymer binder or conductive additives. Germanium was chosen as the active material in our monolith anode not only for its capacity ability (1600 mA h g\(^{-1}\), corresponding to Li\(_{1.5}\)Ge\(_2\)), but also for its excellent lithium-ion diffusivity (400 times faster than Si) and high electrical conductivity (10\(^4\) times higher than Si).\(^{14}\) All these advantages make germanium a promising alternative material for a graphite anode. However, most of the present routes for synthesizing Ge materials employ organic Ge sources such as...
germane (GeH₄), germanium tetrachloride (GeCl₄) and phenyltrimethylgermane (C₉H₁₄Ge). The high cost of Ge salts limits their large-scale application in LIBs. For this reason, germanium dioxide (GeO₂) is a promising precursor to prepare Ge materials. In this study, Ge particles were synthesized via a facile solution route using GeO₂ as a precursor.

It is worth mentioning that the CNT conductive network, which in situ grows on the surface of copper foams, plays an important role in this unique structure. On the one hand, the highly conductive CNT network provides an efficient pathway for electrons migrating from the Ge particles to the Cu current collector. On the other hand, the liquid electrolyte can easily soak into the electrode due to its porous structure and a fast Li ion transport could be realized. More importantly, due to the excellent mechanical strength, the well-connected CNT skeleton acts as a fantastic elastic buffer, which could accommodate a metallic Ge expansion when Li ions enter. Thereby the structure of the electrode would maintain itself during cycling and a stable energy delivery could be expected.

A typical procedure for the synthesis of the Ge–CNTs–Cu foam monolith anode is shown in Scheme 1. Initially, the Cu foam substrate was coated with CNTs via a simple catalytic growth using Cu nanoparticles as the catalyst. It is clearly seen that the randomly grown multi-walled CNTs covered the Cu foam substrate completely (Fig. S1 of ESI†). Then, the Ge precursor was prepared by a wet-chemistry method at room temperature. The as-synthesized Ge powder was loaded in an alumina boat and covered with the CNT coated Cu substrate. After heat-treatment at 600 °C for 1 h in an H₂ atmosphere, Ge particles were directly grown onto the CNT network and the Ge–CNTs–Cu monolith anode was finally obtained. Electrochemical experiments were performed using a two-electrode Swagelok cell with Lithium foil and glass fiber as the counter electrode and separator, respectively. The low cost of the precursor and the mild preparation conditions make this 3D conductive anode a promising candidate for a lithium-ion battery anode.

Fig. 1 shows the X-ray diffraction (XRD) pattern and Raman spectrum of the 3D Ge–CNTs–Cu anode. There are five peaks observed in the XRD pattern (Fig. 1a) that can be indexed to the cubic phase of Ge (JCPDS 04-0545), which demonstrate the presence of crystal Ge in our composite electrode. Besides the peaks corresponding to the Cu substrate, a Cu₃Ge alloy signal is also observed in the XRD pattern, which may be ascribed to the reaction between the Ge and Cu nanoparticles at high temperature. Although the Cu₃Ge phase does not react with Li, the alloy is reported to be an excellent electron conductor with a much higher electrical conductivity [(1.00–1.67) × 10⁷ S m⁻¹] than that of pure Ge (1.45 S m⁻¹), which may be favorable for electron transfer during an electrochemical reaction. Further structural information is provided by the Raman spectrum in Fig. 1b. Similar to our previous studies, there are three strong peaks detected, in which the sharp peak located at 297.2 cm⁻¹ represents the optical mode of crystalline Ge, and the other two broad peaks can be attributed to the disorder-induced D band at 1330 cm⁻¹ and the graphitic G band at 1600 cm⁻¹ due to the contribution of the CNT framework. The weak peak located at 554 cm⁻¹ can be interpreted as the strong resonance of two-photon pairs.

Scanning electron microscopy (SEM) is employed to verify the morphology of the Ge–CNTs–Cu monolith anode. As is shown in Fig. 2a, randomly oriented CNTs grow and cover the surface of the Cu foam current collector to construct a fast electron transfer framework. Ge particles with sizes around 500 nm are embedded uniformly in the conductive skeleton formed by the CNTs (Fig. 2b–

**Scheme 1** Schematic illustration of the preparation of the Ge–CNTs–Cu monolith anode.
c). The corresponding element mapping images in Fig. 2d–e further confirm the uniform distribution of Ge and C in the 3D anode. The unique structure of tightly linked active Ge particles and the elastic CNT networks may be expected to be responsible for the beneficial cycling performance, as well as the improved mechanical property of the electrode.

The electrochemical performance of the Ge–CNTs–Cu monolith anode are shown in Fig. 3 with all the specific capacities calculated based on the total electrochemical active electrode mass, including the Ge particles and CNTs. As a comparison, a bare Ge electrode was also checked in Fig. S2 of the ESI†. As shown in Fig. S2a–b of the ESI†, the bare Ge electrode exhibits a relatively low coulombic efficiency (28%) and undergoes a rapid specific discharge capacity fade which decreases from 965 mA h g\(^{-1}\) to 350 mA h g\(^{-1}\) after ten cycles. The unstable fresh active surface generated by the bare Ge continuously reacted with the electrolyte, which may account for the capacity decay as reported in the literature.\(^{5a,7a,17}\)

However, for our 3D Ge–CNTs–Cu anode, it is clear from Fig. 3a that there is a very long voltage plateau around 0.3 V which may be ascribed to the formation of a Li\(_3\)Ge alloy.\(^{1}\) The discharge and charge capacity of the first cycle were 1134 mA h g\(^{-1}\) and 887 mA h g\(^{-1}\), respectively, corresponding to a coulombic efficiency of 78%, which is similar to previous literature.\(^{5a,11b}\) The solid electrolyte interface (SEI) formed by the side reaction between the active material and the electrolyte, as well as the trapped Li ion inside the anode, may be responsible for the irreversible capacity.\(^{5a,11c,16}\)

Improved cycle performance was also exhibited by our 3D Ge–CNTs–Cu anode. The discharge capacity for our novel anode remained 800 mA h g\(^{-1}\) after a 100 discharge/charge cycles at a current density of 150 mA g\(^{-1}\), which is much higher than that of a bare Ge electrode (Fig. S2b, ESI†). This stable energy delivery may be benefited from the unique structure of the monolith anode. Firstly, the existence of a nanospace created by the cross linked CNTs accommodates the alloyed Ge particles. More importantly, when the alloy reaction occurs during the discharge process, the CNT network may provide a powerful elastic buffer which could limit the excessive volume expansion of Ge. Additionally, for the Ge–CNTs–Cu anode, CNTs act as a conductive medium between the active Ge particles and the Cu current collector when the electrochemical reaction occurs. A fast electron transfer could be realized in the unique 3D structure, and consequently this leads to an improvement in the rate capability, as well as an improved voltage hysteresis between charge and discharge, in contrast to the Ge–Cu anode (Fig. S2, ESI†). It is known that small voltage hysteresis is favorable for batteries to achieve high energy efficiency, a high energy density when using our elastic Ge–CNTs–Cu monolith as a LIB anode would be expected.

As is shown in Fig. 3c, the 3D Ge–CNTs–Cu anode exhibits reversible discharge capacities of 719 mA h g\(^{-1}\), 533 mA h g\(^{-1}\) and 398 mA h g\(^{-1}\) when the current densities increase from 300 mA g\(^{-1}\) to 600 mA g\(^{-1}\) and 900 mA g\(^{-1}\).

The improved Li ion transfer performance in the novel Ge–CNTs–Cu monolith anode is also confirmed by the electrochemical impedance measurements before and after the discharge/charge cycles. It can be clearly seen from the Nyquist plot shown in Fig. 4 that the cell resistance of the battery with the Ge–CNTs–Cu monolith anode is much lower than that of the Ge–Cu electrode (Fig. S3, ESI†). This is convincing evidence for a fast electron migration in a composite electrode due to the existence of CNTs as a conductive medium. Specifically, there are two semicircles in the high and middle frequency regions for our monolith anode, however, there is only one for the bare Ge–Cu anode. The RC equivalent circuit models and fitting values in Table S1 of the ESI† show that there are two additional circuit elements, R\(_t\) and C\(_t\), in the equivalent circuit model of the Ge–CNTs–Cu monolith anode. And this may be attributed to the contact interface formed by Ge.
and CNTs, which is similar to the results observed in the sandwiched nanotube–Cu$_2$O$_3$–Cu composites. After 10 discharge/charge cycles at a current density of 150 mA g$^{-1}$, the charge transfer resistance ($R_e$) of the 3D anode decreased from 160.1 $\Omega$ to 40.77 $\Omega$ and this was due to the formation of a favorable SEI which was believed to be beneficial to the Li ion transfer at the interface between the electrolyte and the electrode. Both the constant phase elements ($C_1$ and $C_2$) increased gradually after cycling, implying a more capacitive interface formed by the CNTs.

In conclusion, we explored an elastic Ge–CNTs–Cu foam monolith as a rechargeable lithium battery anode without any polymer binder or additives. It is demonstrated that an enhanced cycle performance can be acquired because the conductive CNTs accelerate the electron diffusion from Ge active particles to the copper foam current collector and the elastic CNT framework buffers the expansion of Ge particles, which maintain a good structural integrity. A low cost Ge precursor and mild preparation conditions, as well as the unique electrode structure, endow this 3D elastic monolith as a promising candidate for the anode of lithium batteries. The design of a 3D elastic monolith might open up opportunities to exploit alloy anode materials with high capacities.

Acknowledgements

This work was supported by the key Research Program of the Chinese Academy of Sciences (Grant No. KGZD-EW-202-2), the “100 Talents” program of the Chinese Academy of Sciences, the National Program on Key Basic Research Project of China (973 Program) (No. MOST2011CB935700), the National Natural Science Foundation of China (Grant No. 20901077, 20901044, and 20902052) and the Shandong Province Fund for Distinguished Young Scientist (JQ200906).

References