



# Composite Li metal anode with vertical graphene host for high performance Li-S batteries

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## HIGHLIGHTS

- Vertical graphene composite Li anodes are fabricated by melt-infusion method.
- Lithiophilic Si layer is coated to assist this melt-infusion process.
- The composite electrodes exhibit good stability in symmetric lithium batteries.
- The composite electrodes display enhanced cycling reversibility in Li-S system.

## ARTICLE INFO

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## ABSTRACT

Efficient and stable operation of a lithium metal anode has become the enabling factor for next-generation high energy density storage system. Here, vertical graphene (VG) arrays are used as the scaffold structure for high performance Li metal batteries. The melt infusion method is employed to encapsulate Li inside the VG scaffold structure, and the lithiophilic Si layer is coated onto the array surface by magnetron sputtering to assist this melt-infusion process. The porous scaffold structure can control the volume expansion and inhibit the formation of dendritic lithium significantly, leading to the excellent electrochemical performance of the Li composite anode. In addition, the Li-S full batteries with the composite anode display enhanced cycling reversibility.

## 1. Introduction

The earliest commercial products of rechargeable Li batteries appeared in the 1970s were quickly discarded because the safety hazards and catastrophic failure occurred due to the dendritic growth and virtually relative infinity volume change during long-term cycling [1–8]. Since the commercialization of Li-ion batteries (LIBs) in the 1990s, they have attracted great interest and now dominate the market for powering electric vehicles and commercial electronics such as smart phones and laptops. However, the enhanced battery safety of LIBs is at a significant cost of energy density. Recently, the high energy density Li metal anodes have been world-widely investigated again because of their irreplaceable position in the “next generation” rechargeable batteries, such as Li-air and Li-S batteries [9–13]. The lowest negative electrochemical potential ( $-3.045$  V vs. standard hydrogen electrode (SHE)), high theoretical specific capacity ( $3860$  mAh  $g^{-1}$ ) and low

density ( $0.59$  g  $cm^{-3}$ ) of Li metal anodes will lead to a revolution in new energy field, and the progress of science technology provides the possibility to solve the safety hazards existed [14,15].

To date, well known challenges with Li metal anodes still remain: (1) safety issues associated with the formation of dendrite Li, (2) unstable solid electrolyte interphase (SEI) due to the highly reactive nature of Li metal, and (3) low Coulombic efficiency upon cycling [16–18]. To circumvent these problems, numerous strategies were employed, including optimizing electrolyte components [19,20], fabricating an artificial SEI [21–25], building a scaffold structure [26–29], and using advanced separator [30].

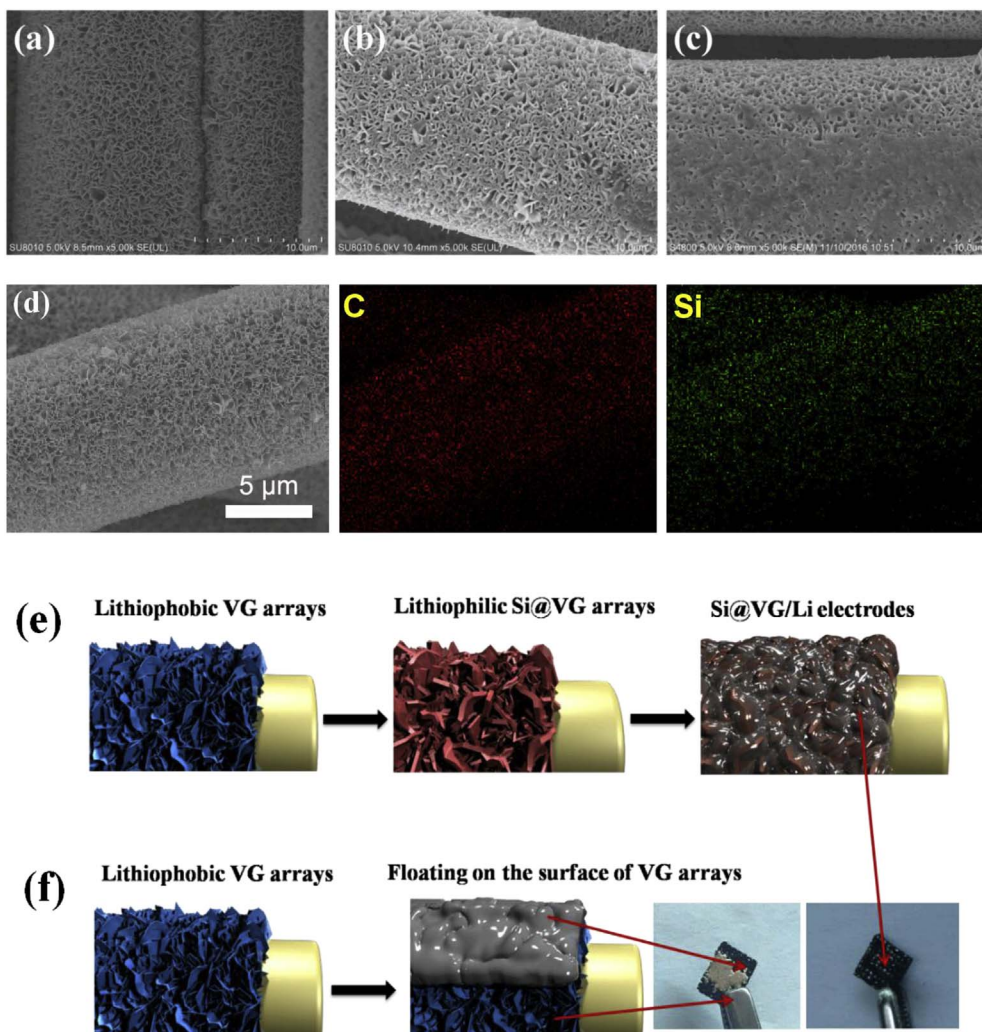
Here, a stable lithium-scaffold composite electrode is developed by melt infusion method. According to previous reports, several kinds of scaffold structure are applied to plating of metallic lithium, such as 3D-graphene framework [31], porous graphene network [26,28], 3D porous carbon matrix [32] and so on. These dual-phase lithium metal

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**Fig. 1.** SEM images of VG arrays (a), Si@VG arrays (b) and Si@VG/Li electrodes (c); (d) EDS elemental mapping images of C, Si for Si@VG; (e) (f) the mechanism diagram of melt-infusion process of “lithiophilic” Si@VG arrays and “lithiophobic” VG arrays, respectively.

anodes can act as caged entrapment for lithium metal within the interior of the scaffold structure, and serve as a rigid host with Li uniformly confined inside to accommodate the electrode-level virtually infinite volume change of Li metal during cycling. The cycling performance of symmetric lithium cells is improved and the dendrite formation is suppressed. Compared with many of the battery electrodes which can be fabricated via various synthetic processes, how to encapsulate more metal Li inside the scaffold structure presents a major challenge. As metal Li will melt into liquid when heated above 180 °C, melt infusion is the most promising method to achieve this aim. The VG arrays without surface modification present a “lithiophobic” character and the molten Li cannot flow into it. To solve the “lithiophobic” effect between the vertical graphene (VG) arrays and liquefied Li, the “lithiophilic” Si layer is coated onto the surface of VG arrays by magnetron sputtering to assist this melt-infusion process. As a result, the molten Li can easily and quickly flow into the Si coated VG arrays and occupies the interspaces between each graphene sheet to form the Si@VG/Li electrodes.

## 2. Experimental

### 2.1. Fabrication of Si@VG/Li electrode

In this work, microwave plasma enhanced chemical vapor deposition (MPECVD) was applied to synthesize the VG arrays on carbon cloth

similar to references [33,34]. Firstly, the Si layer was deposited onto the VG arrays by magnetron sputtering method. Prior to deposition, the base pressure of the sputtering system was evacuated to  $4 \times 10^{-3}$  Pa, and then argon gas was introduced to keep the working pressure of 0.2 Pa. In order to remove the oxides and adsorptions, the substrates were etched by  $\text{Ar}^+$  bombardment at a negative bias of 500 V for 30 min. During the deposition process, the current of graphite targets was kept at 1 A, and the sputtering bias was maintained at 50 V. After the magnetron sputtering, the Si@VG composite arrays were obtained. Secondly, the Li foil was heated above its melting temperature under argon atmosphere, and the resulting molten Li can be absorbed into the scaffold rapidly because the Si layer on VG arrays could cause the scaffold surface to switch from “superlithiophobic” to “superlithiophilic” behavior [30]. As a result, the Si@VG/Li composite anodes were fabricated successfully.

### 2.2. Characterization and electrochemical measurement

The surface morphologies and element distribution of electrodes before and after cycling were observed using scanning electron microscope (SEM, Hitachi S-4800 equipped with GENESIS 4000 EDAX detector). To avoid air contamination, the Li electrode samples were transferred in the sealed box filled with argon gas and loaded into the machine under pure argon atmosphere.

Coin-type cells (CR 2025) were assembled in an argon-filled glove to

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