Self-assembled asymmetric membrane containing micron-size germanium for high capacity lithium ion batteries†

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Here we report the formation of novel asymmetric membrane electrode containing micron-size (~5 μm) germanium powders through a self-assembly phase inversion method for high capacity lithium ion battery anode. 850 mA h g⁻¹ capacity (70%) can be retained at a current density of 600 mA g⁻¹ after 100 cycles with excellent rate performance. Such a high retention rate has rarely been seen for pristine micron-size germanium anodes. Scanning electron microscope studies reveal that germanium powders are uniformly embedded in a networking porous structure consisting of both nanopores and macropores. It is believed that such a unique porous structure can efficiently accommodate the ~260% volume change during germanium alloying and de-alloying process, resulting in an enhanced cycling performance. These porous membrane electrodes can be manufactured in large scale using a roll-to-roll processing method.

Introduction

High capacity lithium ion batteries (LIBs) have broad applications from static energy storage of intermittent power sources, mobile electronics to electric vehicles.¹⁻⁴ Commercial graphite anode for rechargeable LIBs has a limited theoretical capacity of 372 mA h g⁻¹.² To further increase the overall capacity of LIBs, alloying anode materials such as silicon and germanium have been extensively explored, mainly due to their attractive high theoretical capacities.⁴⁻⁸ Compared to silicon, Ge has several advantages as a LIB anode: (1) several orders of magnitude higher in electrical conductivity and lithium ion diffusivity enabling excellent rate performance;⁷ (2) particles more robust and thus lower tendency to fracture with similar particle size during the repeating lithiation/de-lithiation process, which has been revealed by recent in situ transmission electron microscopy (TEM) studies;¹⁰⁻¹² (3) similar volumetric capacities (7366 A h L⁻¹ for Ge vs. 8334 A h L⁻¹ for Si).⁸

However, Ge, similar to Si, experiences immense volume change (~260%) during lithium intercalation and de-intercalation, which induces huge stress leading to fracture, pulverize, and lose contact with conductive additives. Additionally the unstable solid electrolyte interphase (SEI) consumes lithium metal continuously, leading to a dramatic capacity fade. Quite a few creative strategies have been proposed to overcome the aforementioned volume expansion problem, mainly through various kinds of nanostructuring (nanowires, nanotubes, nanoparticles, microporous and mesoporous materials).⁵⁻¹⁷ However, expensive chemical vapour deposition (CVD) technology, risky acid etching, complicated metal reduction and costly catalysts are usually needed to obtain these nanostructures, thus hindering their practical application in large scale. Further, nanomaterials are orders of magnitude more expensive than their micron-size counterparts. Therefore, it is highly desired to use micron-size Ge and Si powders in LIBs. Unfortunately, the cycling performance of micron-size Si and Ge is extremely poor, and very few successful cases have been reported so far.¹⁸⁻²⁰ Cui et al. utilized various glues to enhance the cycling performance of micron-size silicon using either extremely thin coating (~3 μm thick)²⁰ or only charging the silicon anode partially (~1200 mA h g⁻¹).¹⁸ What is needed in research is to develop a scalable method to synthesize micron-size germanium-based anode materials with reasonable thickness (~100 μm) for practical applications, which can also be charged and discharged to its full capacity with satisfying cycling performance.

Asymmetric reverse osmosis (RO) and nanofiltration (NF) membranes are playing an important role in our daily life by providing billions of tons of desalinized water worldwide annually.²¹ These membranes are characteristic of robust asymmetric porous structure consisting of interconnecting nanopores and macropores,²² which characteristic can be utilized to solve the volume expansion problem of alloying anode materials, e.g., Si and Ge, for next generation high

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capacity lithium ion battery (LIB). In addition, these membranes can be fabricated in large scale with highly controllable thickness using a well-established roll-to-roll process via a self-assembly phase inversion mechanism. Such an excellent scalability is highly desirable for practical applications in battery industry. In phase inversion process, a homogeneous polymeric solution is immersed into a non-solvent. The polymer has negligible solubility in the non-solvent, while the non-solvent and solvent are miscible with each other. Then de-mixing will occur, resulting in the formation of two phases (polymer-lean and polymer-rich) and the spontaneous generation of asymmetric porous structure (Fig. 1d). It is called ‘asymmetric membrane’ because these membranes consist of a top nano-porous layer and a bottom macro-porous layer (Fig. 1a). On the top surface, the polymeric solution is in contact with large quantity of non-solvent, leading to a fast de-mixing and quick precipitation of polymer. Thereby the top surface is relatively dense. In stark contrast, the solvent in the bottom layer of polymeric solution is slowly de-mixing with non-solvent, causing the formation of macro-porous structure.

In this report, the scalable membrane technology is adapted to produce polysulfone/Ge composite membranes using Ge micron-size powders as the starting material. These composite membranes are then carbonized to form Ge–C inorganic asymmetric membranes for high performance LIB anodes. These membrane electrodes demonstrate excellent rate and cycling performance owing to the robust interconnecting porous structure and high electrical conductivity. This work is distinguished from other methods in simplicity, efficiency and high scalability.

Results and discussion
Design and fabrication of Ge asymmetric membrane for lithium ion anodes

Due to the large volume change (~260%) and poor mechanical strength, LIB anodes made of micron-size Ge powders have unsatisfying cycling life. Various kinds of nano-structuring (nanowires and nanoparticles) have been proposed to stabilize Ge-based alloying anode. However the manufacturing cost of nanomaterials can be several orders of magnitude higher than micron-size materials because of the use of costly chemical vapor deposition (CVD) technique, expensive catalysts and complex templating methods as mentioned above. Further, graphene, carbon nanotubes and non-conventional binders are usually needed during the preparation of Ge nanoparticles (NPs)-based electrodes. All these facts can significantly hinder their practical applications in large scale. So what is needed is to create a new synthetic route to obtain stable Ge electrodes using micron-size powders as the raw material, thus substantially reducing the cost. Polymeric asymmetric membranes can be fabricated in large scale via a self-assembly phase inversion mechanism. During the phase inversion, a homogeneous polymeric solution of single phase is immersed into a non-solvent, leading to de-mixing and spontaneous formation of asymmetric porous structure. Herein we adapted this amazingly facile method to make inorganic Ge asymmetric membranes for efficient lithium storage.

As-received Ge powders (~100 μm) were ground to ~5 μm using a ball mill before being used for the membrane fabrication (S1†). This grinding process is necessary because 100 μm particles can settle quickly to the bottom of container due to the effect of gravity, resulting in their separation from the polymeric solution. Ground Ge powders were mixed with carbon black and polysulfone dissolved in N-methyl-2-pyrrolidone (NMP), which was then used for the phase inversion. NMP, water and polysulfone (PS) are employed as solvent, non-solvent and polymer, respectively. Carbon black (CB) is utilized as a filler to increase the electrical conductivity and adjust content of active material Ge powders in the membrane to reduce the overall volume expansion. These inorganic/polymeric membranes were fabricated via the self-assembly phase inversion technique and their comprehensive properties are then systematically evaluated.
carbonized to obtain conductive Ge membranes for LIB anode. Noteworthy, the top dense layer can help prevent the pulverized germanium particles from being leaked out into electrolytes, which can cause rapid and permanent capacity loss. The bottom porous layer can function as a robust mechanical support and allow for the large volume expansion. Further, the layer of carbon film coated on Ge powders can assist the formation of a stable SEI layer and favor a longer cycle life.\textsuperscript{32,33} It is notable this method can be easily scaled up as evident by the 13-inch long Ge asymmetric membrane prepared using a large glass plate as the substrate (Fig. 1). With roll-to-roll processing facilities in membrane industry, these membranes can be produced continuously in large quantities.

Characterization of germanium asymmetric membranes

As-received Ge powders have a broad size distribution ranging from several microns to hundreds of microns (S1\textsuperscript{†}). After the grinding process, the size of Ge powders is reduced to 5 \textmu m on average (S1\textsuperscript{†}). Since these Ge powders have irregular shapes, we use Heywood diameter to represent their size, which was calculated as \(d_p = 2\sqrt{A/\pi}\). Heywood diameter, \(d_p\), is the equivalent diameter of the circle that has the same area as the projected area (A) of Ge particle from TEM image (S1\textsuperscript{†}). The average Heywood diameter is 5.0 \textmu m with a standard deviation of 3.2 \textmu m. In comparison CB NPs are much more uniform with an average diameter of \(\sim 56.4\) nm and a standard deviation of \(\sim 15.7\) nm (S1\textsuperscript{†}). Scanning electron microscope (SEM) imaging confirms the formation of porous structure after the phase inversion process (Fig. 2 and S2\textsuperscript{†}).

These Ge micron powders (MPs) are uniformly dispersed in the porous carbon networks (Fig. 2 and S2\textsuperscript{†}). For Ge asymmetric membrane of 100 \textmu m wet coating thickness (Ge 15WT100M), the membrane shrank to 53 \textmu m after the phase inversion because the solvent is de-mixed. After being carbonized at 800 °C for 2 h, the membrane thickness was further reduced by 40\% to 32 \textmu m (Fig. 2). For Ge asymmetric membrane of 250 \textmu m wet thickness, the membrane thickness after the phase inversion is 138 \textmu m, which was decreased to 43 \textmu m after the carbonization (Fig. 2).

The sharp Raman peak centered at 315 cm\(^{-1}\) for Ge micron powders and Ge asymmetric membranes carbonized at 800 °C for 2 h can be attributed to the phonon scattering of bulk Ge (Fig. 3a).\textsuperscript{34,35} G and D Raman peaks from graphitic materials can also be seen in these carbonized Ge asymmetric membranes (Fig. 3a). The low G/D ratio indicates these graphitic materials were not of high crystallinity, which is not surprising due to the low carbonization temperature (800 °C). Powder X-ray diffraction data confirms the presence of crystalline cubic Ge in these carbonized Ge asymmetric membranes (Fig. 3b). The weak pattern at \(\sim 26°\) is from poorly crystallized graphite, which is also consistent with the low G/D ratio in Raman spectra (Fig. 3a and b).\textsuperscript{36} Surface area analysis further verifies the presence of porous structure in these Ge asymmetric membranes (Ge 15WT100M) with a specific area of 132 m\(^2\) g\(^{-1}\) calculated using Brunauer–Emmett–Teller (BET) method (Fig. 3c). These pores have a wide size distribution as proved by Barrett-Joyner-Halenda pore size distribution data (Fig. 3d). The broad size distribution of Ge asymmetric membrane (Ge 15WT100M) and Ge asymmetric membranes (Ge 15WT250M and Ge 15WT100M); (c) BET surface area; and (d) BJH pore size distribution of Ge asymmetric membrane (Ge 15WT100M). Note: * is the XRD pattern from graphitic materials (JCPDS Card no. 75-1621) and ++ represents XRD patterns from cubic phase (JCPDS no. 04-0545). All membranes were carbonized at 800 °C for 2 h.

\begin{figure}[h]
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\caption{SEM images of (a) Ge asymmetric membrane before carbonization (Ge 15WT100M, 100 \textmu m wet thickness); (b) Ge asymmetric membrane after carbonization at 800 °C for 2 h (Ge 15WT100M, 100 \textmu m wet thickness); (c) Ge asymmetric membrane before carbonization (Ge 15WT250M, 250 \textmu m wet thickness); (d) Ge asymmetric membrane after carbonization at 800 °C for 2 h (Ge 15WT250M, 250 \textmu m wet thickness). Note: all images are cross-section view.}
\end{figure}
distribution is also consistent with the SEM imaging and its intrinsic asymmetric structure (Fig. 3d).

The content of active material germanium in these carbonized asymmetric membranes was determined using thermogravimetric (TGA) analysis (Fig. 4) based on an assumption that germanium and carbon can be fully oxidized to GeO₂ (s) and CO₂ (g) in air, respectively. This assumption is validated by TGA data. As shown in Fig. 4, the mass percentage of pure Ge is increased by 40.1%, indicating the formation of GeO₂. Theoretically, the mass percentage should be increased by 44% if Ge is fully oxidized to GeO₂. The slight difference from theoretical value is probably due to the trivial oxidation of Ge powders during the grinding process. As for carbonized PS/CB membrane, its mass is decreased by 99.8% during the TGA analysis because it is completely oxidized into CO₂ gas. Based on this assumption, the contents of germanium were calculated to be 53.3 and 57.1 wt% in Ge asymmetric membranes of 100 and 250 μm wet thicknesses (Ge 15WT100M and 15WT250M), respectively.

**Electrochemical properties of Ge and Ge/carbon black asymmetric membranes as LIB anodes**

The de-lithiation capacity of Ge asymmetric membranes carbonized at 800 °C for 2 h with a wet thickness of 100 μm is as high as 1700 mA h g⁻¹ at a current density of 200 mA g⁻¹ based on germanium (Fig. 5a and e), which is very close to the value reported by Fultz et al. The capacity based on overall membrane mass is ~940 mA h g⁻¹, which is nearly three times higher than commercial graphite electrodes (Fig. 5e). The electrodes also exhibit excellent rate performance. When applying a current density of 800 mA g⁻¹, nearly 66% (1129 mA h g⁻¹ based on Ge mass or 620 mA h g⁻¹ based on overall membrane mass) capacity can be retained as compared to 200 mA g⁻¹ (Fig. 5e). Noteworthy, the lithiation and de-lithiation current densities are identical. Such an excellent rate performance can be attributed to the networking carbon structure and high porosity, which allow for excellent electrical conductivity and short lithium ion diffusion length.

Germanium asymmetric membrane electrodes also demonstrate an outstanding cyclability as compared to other micron-size germanium anodes which are not specially treated to obtain nanoscale sub-structures. 70% capacity (850 mA h g⁻¹ based on Ge mass or 467 mA h g⁻¹ based on overall membrane mass) can be retained after 100 cycles at 600 mA g⁻¹ based on Ge mass with a coulombic efficiency ranging from 99–100% (Fig. 5a and c). After deducting the capacity from carbon black and carbonized polysulfone (~200 mA h⁻¹ on average), it is still above 750 mA h g⁻¹ based on Ge mass (Fig. 5a and c). The capacity is also plotted as normalized to the total electrode weight in Fig. 5c and e, which provide more information on the overall electrode performance. Although the capacity is much lower when normalized to the total electrode weight, it is still much higher than graphite anode. Noteworthy the capacity could be further increased with optimization of electrode
formulation. It is believed the solid asymmetric porous structure can stand the huge stress generated during the germanium lithiation/de-lithiation processes. Furthermore, fractured Ge powders can be retained in these interlinking nanopores and macropores without being leaked out into the electrolytes and losing capacity rapidly.

During the first formation cycle of 100 μm Ge asymmetric membrane, there are two sharp peaks at 0.21 V and 0.51 V (S3†), which can be assigned to the insertion and extraction of lithium in crystalline germanium, respectively.38 In the second and third formation cycles, these two peaks are changed to two broad ones centered at 0.20 V and 0.60 V, respectively, which is due to the insertion and extraction of lithium into amorphized Ge and is common in germanium anode materials.39 The initial capacity losses (ICL) of Ge asymmetric membranes are 26% and 30%, respectively, for membranes with wet thicknesses of 100 and 250 μm, respectively. These ICL values are again very comparable to other Ge-based LIB anodes.16,40 Thickness of Ge asymmetric membranes has a certain impact on their cycling performance (Fig. 5a). When the thickness is reduced from 250 to 100 μm (wet membrane thickness), retention rate is improved from 63% to ~70% in 100 cycles. It is probable that the stress in thicker membrane electrode is higher than thinner one, thus tending to destroy the porous structure more easily.

Pure germanium powder electrode is extremely unstable as evidenced by the quick degradation in capacity that was decreased below 100 mA h g⁻¹ in less than ten cycles (Fig. 5a and b). Lu, et al. reported the stability of germanium oxide thin film electrode is in reverse proportion to its particle size. For macro-size GeO₂, its initial capacity is only 225 mA h g⁻¹, 30% of which can be retained in 10 cycles.41 Their data are quite consistent with our pure germanium powder electrode data. In contrast carbonized polysulfone and carbon black membrane (PS/CB 15WT250M) without germanium powders shows an excellent cyclability, but unfortunately its capacity is too low (~200 mA h g⁻¹) similar to literature report.42

**Experimental**

**Synthesis of germanium asymmetric membranes using micron-size Ge powders**

As-received Ge powders (Alfa Aesar, 100 meshes, 99.999%) were ground for 8 h at 30 rpm using a planetary ball mill mixer (Across International, PQ-N04) before being used for the membrane fabrication. Next, 1.0 g ball-milled Ge powders (an average size of ~5 μm), 0.40 g carbon black (TIMCAL SUPER C45 with a surface area of 45 m² g⁻¹) and 1.5 g polysulfone (Mₙ = 22 000, Sigma Aldrich) were dispersed in 10 mL N-methyl-2-pyrrollidone (NMP) (Sigma Aldrich, >99.5%). The solution was mixed thoroughly by vortexing (Barnstead International) for 30 minutes and sonication (Bransonic CPX3800H) for 1 h. Next, the suspension was coated onto a piece of silicon (100) wafer of 2 inches in diameter using a doctor blade with a wet membrane thickness of either 250 μm or 100 μm. The coated wafer was immersed into ethanol for 30 minutes to form asymmetric membrane. Finally, the membrane was carbonized at 800 °C for 2 h using a Lindberg/Blue M™ 1100 °C tube furnace with a ramp of ~60 °C min⁻¹. High purity helium gas (99.9999%, Airgas He UHP300) was flown at 200 sccm to prevent oxidation of Ge and carbon. The membranes were labeled as Ge 15WT250M and Ge 15WT100M for wet membrane thicknesses of 250 and 100 μm, respectively. It should be pointed out specifically that asymmetric membrane structure can’t be maintained after being carbonized without the addition of carbon black as the filler to support the backbone of the porous structure. The addition of carbon black also benefits the electron transfer and reduces the overall volume change of asymmetric membrane during lithiation/de-lithiation process.

**Synthesis of asymmetric membranes without Ge powders**

Membranes without Ge powders were also fabricated using the aforementioned method for control experiment, which had a wet membrane thickness of 250 μm and were carbonized at 800 °C for 2 h. The control membrane sample was labeled as PS/CB 15WT250M herein.

**Characterization**

A field emission electron microscopy (JEOL JSM-7600F) attached with Transmission Electron Detector (TED) at Georgia Southern University was utilized for morphology and structural characterization. A Thermo Scientific DXR SmartRaman Spectrometer in Prof. Rafael Quirino labs at Georgia Southern University was used for phase identification. The power of the laser is 3 mW of 532 nm wavelength and the objective lens is ×10 with a total integration time of 100 seconds. Samples were also characterized using powder X-ray diffractometer (Scintag XGEN-4000) using a Cu Kα radiation (λ = 1.542 Å) from 10 to 80° with a step rate of 0.03° s⁻¹. The acceleration voltage and current are 40 kV and 40 mA, respectively with a step rate of 0.03° s⁻¹. A Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer was employed to measure the specific surface area and pore size distribution. They were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Membrane samples were degassed at 50 μTorr and 300 °C for 30 minutes before N₂ gas adsorption and de-adsorption measurements. The nitrogen adsorption and desorption isotherms were collected at 77 K using ultrahigh purity N₂ gas (Airgas UHP300, 99.9999%). The content of germanium was determined by a thermogravimetric analyzer (NETXSCH STA 449 F3) using compressed air as the purging gas (Ultra Zero, Airgas). The flow rate of compressed air gas is 40 mL min⁻¹ and the temperature is ramped at a rate of 10 °C min⁻¹.

**Electrochemical evaluation of germanium asymmetric membranes as LIB anodes**

Ge asymmetric membrane was glued directly onto a piece of copper disc (15 mm in diameter and 11 μm thick from MTI Corporation). The glue was made of 0.1 g carbon black and 0.1 g polyvinylidene difluoride (PVDF, MTI Corporation) dissolved in 3 mL NMP. The uncalendered electrode was then dried under vacuum at 120 °C overnight to remove NMP and H₂O moisture. The final mass of active material on the copper disc was ~1.0
mg. The electrode was then assembled into 2032-type coin cells using lithium metal (EQ-Lib-LiC25, MTI Corporation) as the counter electrode and 1 M LiPF₆ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with a volume ratio of 1 : 1 : 1 (MTI Corporation) as the electrolyte. Inside the glove box (LCPW, LC Technology Solutions, Inc.), oxygen and water concentrations were maintained below 1 ppm. The membrane separator was purchased from MTI Corporation (ethylene/polypropylene blend with pore sizes 20–30 nm). Two control samples, ball-milled Ge powders (an average size of ~5 μm) and asymmetric membrane without Ge powders (PS/CB 15WT250M) were also assembled into coin cell batteries for comparison. Asymmetric membrane without Ge powders was assembled into coin cell battery using the same method as the one for Ge asymmetric membrane. In the case of ball-milled Ge powders, they were first mixed with carbon black and PVDF in a mass ratio of 8 : 1 : 1 to make a uniform slurry, and then coated onto a copper disc with a wet thickness of 100 μm. Other steps are same as those for Ge asymmetric membrane electrode. Galvanostatic cycling tests of LIB half-cells were conducted using a multi-channel Potentiostat/EIS (BIO-LOGIC VMP3) at 20 °C. The voltage window is 0.01–1.50 V (vs. Li⁺/Li). Three formation cycles at 200 mA g⁻¹ were performed on all LIB cells before any rate and cycling performance tests. Same current densities were applied for both charging and discharging processes for the rate tests.

Conclusions

It is demonstrated that asymmetric porous structure can be utilized as a backbone for lithium-ion battery electrode, where the interconnecting nanopores and macropores mitigates the volume expansion problem of alloy anode materials. This method provides a facile technique toward roll-to-roll manufacturing of high capacity alloy anodes. In addition, it shows that commercially available micron-size Ge powders can be used as the starting material for high capacity LIBs and deliver highly stable cycling performance, which is attributed to the asymmetric porous structure providing both mechanical support and free volume to accommodate Ge lithiation and delithiation with large volume variation. It is also believed that the unique interlinking nanopores and macropores can efficiently prevent the loss of pulverized Ge powders and also enhance the lithium diffusion rate by providing multiple diffusion channels. While the manufacturing process poses commercial potential, challenges remain and further developments in lowing material cost, increasing cycling performance and a real material loading are required.

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