Etching Asymmetric Germanium Membranes with Hydrogen Peroxide for High-Capacity Lithium-Ion Battery Anodes

Ji Wu,* Congrui Jin, Emilee Larson, and Logan Williams

Germanium (Ge) is deemed as one of the most promising alloying anodes for rechargeable lithium-ion batteries (LIBs) due to its large theoretical capacity, high electrical conductivity, fast lithium-ion diffusivity, and mechanical robustness. However, Ge-based anodes suffer from large volume changes during lithiation and delithiation, which can deteriorate their electrochemical performance rapidly. Herein, the large volume change issue is effectively addressed using an asymmetric membrane structure that is prepared using a phase-inversion method in combination with hydrogen peroxide etching and surface coating. The asymmetric Ge membrane etched by \(30\) wt\% \(H_2O_2\) at \(90^\circ\text{C}\) for \(30\) s demonstrates a capacity retention higher than \(80\%\) in \(50\) cycles at \(160\,\text{mA g}\) \(^{-1}\). Coating the \(H_2O_2\)-etched Ge membrane with carbonaceous membranes can further improve the retention up to \(95\%\) in \(50\) cycles at \(160\,\text{mA g}\) \(^{-1}\), whereas \(\approx100\%\) capacity of \(700\,\text{mAh g}\) \(^{-1}\) can be maintained in \(170\) cycles at \(400\,\text{mA g}\) \(^{-1}\). A combination of electron microscopy, spectrophotometry, and X-ray analyses confirms the electrochemical performance of asymmetric Ge membranes as the LIB anode can be significantly affected by membrane geometry, the duration of hydrogen peroxide etching, carbonaceous membrane coating, and Ge concentration.

1. Introduction

High-performance lithium-ion battery (LIB) is crucial to the commercial success of portable electronics, portable power tools, electrical vehicles, and large-scale energy-storage systems for intermittent power sources such as solar, wind, and tide, due to its high energy and power density, long cycle life, negligible memory effect, and environmental benignity.\[^1\] The energy density of commercial LIBs can be further boosted by increasing cell voltage, battery compactness, and electrode capacity.\[^1\] A high electrode capacity could be obtained by simply increasing the thickness of the graphite anode with a theoretical limit of \(372\,\text{mAh g}\) \(^{-1}\). However, entailing gigantic diffusion barriers and large volume changes can seriously impair the cyclability and rate performance.\[^2\]

In contrast, the theoretical capacities of alloying anodes such as Sn (994 mAh g \(^{-1}\)), Si (4200 mAh g \(^{-1}\)), and Ge (1600 mAh g \(^{-1}\)) are from several to tenfolds higher than that of the graphite anode used in state-of-the-art LIBs.\[^3,4\]

In comparison with Si, the most intensively studied alloying anode, Ge does have a few distinguishable advantages: 1) Ge has four orders of magnitude higher electrical conductivity and 400 times faster lithium-ion diffusivity, thus supporting an improved rate performance.\[^5\] 2) The volumetric capacities of Ge and Si are quite comparable with each other (7366 vs 8334 Ah L \(^{-1}\), respectively),\[^5\] and 3) Ge has a lower tendency to be fractured than Si during repeated lithiation/delithiation, as revealed by in situ transmission electron microscopy (TEM) analyses.\[^6\]

However, the large volume change of the Ge-based anode (up to \(260\%\)) can cause electrode delamination, pulverization, and rapid capacity loss. In the past decade, different kinds of nanostructures have been explored to relieve the large volume change issue, including nanowires, nanoparticles, nanoporoporous materials, and nanoscale Ge/C composites.\[^7–10\] Although these nanostructures do enable a much improved electrochemical performance, the high fabrication cost and low scalability may seriously hinder their practical applications.\[^9\] In this regard, it is more cost effective to utilize readily available micrometer-size Ge powders, given that the serious volume expansion issue can be appropriately resolved.\[^11\]

Herein, we present a simple, low-cost, scalable, and effective method to synthesize various asymmetric Ge membranes utilizing micrometer-size Ge powders as raw materials. The asymmetric membranes were fabricated using a straightforward phase-inversion method, followed by hydrogen peroxide etching and surface coating, resulting in an outstanding capacity retention of \(95\%\) at \(\approx850\,\text{mAh g}\) \(^{-1}\) in \(50\) cycles, applying a current density of \(160\,\text{mA g}\) \(^{-1}\), whereas \(\approx100\%\) capacity at \(\approx700\,\text{mAh g}\) \(^{-1}\) can be maintained in \(170\) cycles, applying a current density of \(400\,\text{mA g}\) \(^{-1}\).
2. Experimental Section

2.1. Synthesis of Asymmetric Ge Membranes

2.1.1. Synthesis of Cellulose Acetate Asymmetric Ge Membrane

First, as-received Ge powders (Alfa Aesar, 100 meshes, 99.999%) were ball milled for 2 h at 50 rpm using a planetary ball-mill mixer (Across International, PQ-N04). Second, 1.0 g Ge powders, 0.20 g carbon black (TIMCAL SUPER C45), 0.75 g cellulose acetate propionate (Acros Organics, $M_w = 150,000$), and 5 mL aceton were mixed thoroughly by ball milling at 50 rpm for 2 h to make a uniform slurry. The slurry was then coated into a 200 μm thick film on a silicon wafer (Silicon, Inc. 4 in. (100) Si wafer with a thickness of 1000 μm) using a doctor blade. The thin film was immersed immediately into 100 mL diethyl ether for 30 min at 0 °C to initiate phase inversion, leading to the spontaneous formation of the asymmetric porous membrane. Finally, the membrane was carbonized at 800 °C for 2 h, then at 960 °C for 5 min using a Lindberg/Blue M 1100 °C tube furnace, and under the protection of 200 sccm high-purity helium gas (99.9999%, Airgas He UHP300). The sample was denoted as “CA Ge Mem.”

2.1.2. Synthesis of Polyacrylonitrile Asymmetric Ge Membrane

The synthetic method was similar to the one mentioned previously except that the slurry was made of 1.0 g Ge powders, 0.20 g carbon black, 0.50 g polyacrylonitrile (Platz & Bauer, $M_w = 150,000$), 5 mL N-methyl-2-pyrrolidone (NMP, Sigma Aldrich, >99.5%), and phase inversion was conducted in 1 L deionized water for 10 min. The sample was denoted as “PAN Ge Mem.”

2.1.3. Synthesis of H$_2$O$_2$-Etched Polyacrylonitrile Asymmetric Ge Membrane

PAN Ge Mem was etched by hydrogen peroxide aqueous solutions (Alfa Aesar, 29–32 wt%) at 90 °C for 30 s and 2 min to generate an oxide layer and extra amount of void space, which were denoted as “PAN Ge Mem 30 s” and “PAN Ge Mem 2 min,” respectively.

2.1.4. Synthesis of Dip-Coated H$_2$O$_2$-Etched Polyacrylonitrile Asymmetric Ge Membrane

PAN Ge Mem 30 s was dipped in a slurry that contained 0.50 g PAN, 0.15 g carbon black, and 15 mL NMP and then immersed into 1 L deionized water for 10 min to complete phase inversion. The membrane was dried and carbonized at 800 °C for 30 min to make a sandwich-like membrane, that is, Ge membrane is sandwiched between two layers of porous carbonaceous membranes. The membrane was denoted as “DC PAN Ge Mem 30 s.”

2.1.5. Micrometer Powder Ge Electrode Control

The 0.20 g Ge powders, 0.25 g carbon black, and 0.05 g polyvinylidene fluoride (PVDF, MTI Corporation) were ball milled for 2 h at 50 rpm to make a uniform slurry that was then coated on a copper disc (15 mm in diameter and 11 μm thick from MTI Corporation) using a doctor blade with a thickness setting of 200 μm. The mass percentage of Ge in the control was calculated to be 40 wt%, which is close to the ones in PAN Ge Mem 30 s and DC PAN Ge Mem 30 s.

2.2. Characterization

A field-emission scanning electron microscope (FESEM, JEOL JSM-7600F) attached with an energy-dispersive X-ray analyzer (EDS, OXFORD) and a transmission electron detector (TED) was used for morphological, structural, and compositional characterization. A Thermo Scientific DXR SmartRaman Spectrometer was used for phase identification using 1 mW 532 nm laser, ×10 objective lens, and 120 s integration time to collect the spectra. Samples were also characterized by a powder X-ray diffractometer (PXRD, PANalytical Empyrean) and thermogravimetric analyzer (TGA, TA Instruments Q50 TGA). Powder X-ray diffraction measurements were carried out using Cu Kα radiation ($\lambda = 1.540598$ Å) from 10° to 90° (2θ) with a step rate of 0.1° s$^{-1}$ 32 times to enhance signal-to-noise ratio. The acceleration voltage and current were 40 kV and 40 mA, respectively. High-purity compressed air gas (Ultra Zero, Airgas) at a flow rate of 40 mL min$^{-1}$ was used as the purge gas during TGA analysis. The oven temperature was ramped at a rate from 10°C min$^{-1}$ to 120°C, held for 10 min, and then increased to 700 °C and held for 30 min. The specific surface areas of various Ge asymmetric membranes and micrometer powder Ge were measured using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer at Binghamton University and Brunauer–Emmett–Teller (BET) calculation method. All samples were degassed at 50 μTorr and 300 °C for 30 min before the surface area measurements. Samples were also analyzed using X-ray photoelectron spectroscopy (XPS, Scienta Omicron ESCA-25R) at the Cornell Center for Materials Research Shared Facilities with an operating pressure of $\approx 1 \times 10^{-9}$ Torr. Photocurrents were generated using monochromatic Al Kα X-rays (1486.6 eV) and collected from a 5 mm-diameter analysis area. A hemispherical analyzer was used to determine the electron kinetic energy, using a pass energy of 200 eV for wide/survey scans and 50 eV for high-resolution scans. A flood gun was used for charge neutralization whenever necessary.

2.3. Electrochemical Evaluation of Asymmetric Ge Membranes as LIB Anode

The $\approx 1.0$ mg Ge asymmetric membrane was glued onto a piece of copper disc (15 mm in diameter and 11 μm thick from MTI Corporation) using a slurry composed of 0.15 g carbon black and 0.10 g polyvinylidene difluoride and 3 mL NMP. The electrode was dried at 120 °C for 4 h before being assembled into a 2032-type coin cell using lithium metal (EQ-Lib-LiC25, MTI Corporation) as the counter electrode and 1 M LiPF$_6$ 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 in a glove box (LCPW, LC Technology Solutions, Inc.) with oxygen and water concentrations below 1 ppm.
3. Results and Discussion

3.1. Fabrication of Asymmetric Ge Membranes

Micrometer powder Ge asymmetric membranes were synthesized using a straightforward phase-inversion method.\(^{[7,12]}\) When the polymeric thin film was immersed in the nonsolvent (diethyl ether or water), the solvent (acetone or NMP) was demixed from the polymer (cellulose acetate propionate or polyacrylonitrile) and then mixed with the nonsolvent, resulting in the spontaneous formation of an asymmetric porous structure, that is, the surface layer consists of nanopores, whereas the bottom layer contains macropores. It was reported that the rapid solvent–nonsolvent exchange process at the interface results in the formation of a nanoporous skin layer. Underneath the skin layer, a slower solvent–nonsolvent exchange rate leads to the formation of a macroporous bottom layer.\(^{[13,14]}\) In addition, polymer, carbon black and Ge powders may segregate from each other to form different continuous phases due to the stronger Van der Waals interactions among the same kinds of materials, as pointed out by Zhang and coworkers.\(^{[14]}\) The use of Ge micrometer powders can significantly lower the fabrication cost and thus make this approach more practical for potential commercial applications. The addition of carbon black purposed to increase structural stability and matrix conductivity for enhanced electrochemical properties. It is noteworthy that the slurry must be used immediately after the ball milling to avoid the precipitation of micrometer-sized Ge. Although CA Ge Mem and PAN Ge Mem demonstrated high initial capacities, they deteriorated quickly during the following cycling test. To improve the cycling stability, asymmetric Ge membranes were etched with concentrated \(\text{H}_2\text{O}_2\) solutions to generate extra void space and produce an oxide layer on the micrometer powder Ge core, both of which are beneficial for long-term cyclability. The etched Ge membrane (PAN Ge Mem 30 s) was also coated with carbonaceous membranes to generate a sandwich-like structure, aiming to prohibit the loss of Ge micrometer powders and thereby enhance the cycling performance. The general synthetic strategy of asymmetric Ge membranes and the ternary phase diagram for phase inversion are shown in Figure 1, whose qualitative electrochemical performance is shown in Table 1.

3.2. Characterization of Asymmetric Ge Membranes

SEM images reveal that the Ge membrane made from cellulose acetate propionate (CAP Ge Mem) contains spherical pores, whereas the membrane prepared using polyacrylonitrile (PAN Ge Mem) has finger-like pores (Figure 2a–c). Such a morphological difference is related to the choice of solvent/nonsolvents and polymers, which can affect phase-inversion dynamics.\(^{[13,15]}\) Generally, fast exchange between the solvent and nonsolvent can lead to the formation of finger-like pores (PAN Ge Mem), whereas slow exchange can produce sponge-like macropores (CAP Ge Mem).\(^{[13]}\) EDS elemental mappings (Figure S1, Supporting Information and Figure 3) confirm that Ge powders are uniformly dispersed in the membrane matrix. Etching PAN Ge Mem with concentrated \(\text{H}_2\text{O}_2\) at 90 °C for 30 s (PAN Ge Mem 30 s) can reduce the amount and size of Ge particles on the membrane surface, thus benefiting an improved cycling performance (Figure 2d,e and Figure S1, Supporting Information). Extended \(\text{H}_2\text{O}_2\) etching can eliminate a significant amount of Ge (PAN Ge Mem 2 min). As confirmed by SEM images, EDS mappings (Figure 2f,g and Figure S1, Supporting Information), and TGA analyses, resulting in an extremely low but stable capacity. To prohibit the loss of Ge particles on the membrane surface during repeated lithiation and delithiation, PAN Ge Mem 30 s was coated with carbonaceous, porous membranes (DC PAN Ge Mem 30 s, Figure 2h,i and Figure S1, Supporting Information). The thickness of the carbonaceous membrane...
was estimated to be \( \approx 2 \mu m \) by SEM imaging and EDS line scans (Figure S2, Supporting Information). The SEM image of ball-milled Ge powders is also provided for comparison (Figure S1, Supporting Information, particle sizes range from submicrometer to \( \approx 10 \mu m \)). The thickness of Ge oxide and carbon coating was estimated to be around 100 nm, as shown by TEM images (Figure S1, Supporting Information).

BET surface area analyses (Table 2) indicate that CA Ge Mem and PAN Ge Mem have similar specific surface areas that are 26 and 29 times larger than that of Ge micrometer powders due to the existence of nanopores. The surface area of PAN Ge Mem has been more than doubled after \( \text{H}_2\text{O}_2 \) etching (42.55 and 39.78 m\(^2\) g\(^{-1}\) for PAN Ge Mem 30 s and PAN Ge Mem 2 min, respectively) because the removal of Ge particles on the surface makes the membrane more permeable for N\(_2\) adsorption. DC PAN Ge Mem 30 s possesses the highest specific surface area (91.15 m\(^2\) g\(^{-1}\)) because the carbonaceous membranes are highly nanoporous. Raman spectra (Figure 4a) confirm that CA Ge Mem and PAN Ge Mem are mainly composed of Ge (cubic phase: 293 cm\(^{-1}\))[16] and carbon (G and D peaks: 1590 and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer</th>
<th>Thickness [( \mu m )]</th>
<th>Filler</th>
<th>( \text{H}_2\text{O}_2 ) etching time [s]</th>
<th>Surface coating (Y/N)</th>
<th>Cyclability</th>
<th>Initial capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA Ge Mem</td>
<td>Cellulose acetate propionate</td>
<td>200</td>
<td>Carbon black</td>
<td>0</td>
<td>N</td>
<td>Poor</td>
<td>High</td>
</tr>
<tr>
<td>PAN Ge Mem</td>
<td>Polycrylonitrile</td>
<td>200</td>
<td>Carbon black</td>
<td>0</td>
<td>N</td>
<td>Poor</td>
<td>High</td>
</tr>
<tr>
<td>PAN Ge Mem 30 s</td>
<td>Polycrylonitrile</td>
<td>200</td>
<td>Carbon black</td>
<td>30</td>
<td>N</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>PAN Ge Mem 2 min</td>
<td>Polycrylonitrile</td>
<td>200</td>
<td>Carbon black</td>
<td>120</td>
<td>N</td>
<td>Excellent</td>
<td>Low</td>
</tr>
<tr>
<td>DC PAN Ge Mem 30 s</td>
<td>Polycrylonitrile</td>
<td>200</td>
<td>Carbon black</td>
<td>30</td>
<td>Y</td>
<td>Excellent</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

Table 1. Five types of asymmetric Ge membranes with a different composition, structure, and electrochemical performance.
1350 cm$^{-1}$,[17] and a small amount of trigonal phase GeO$_2$ (116, 162, and 437 cm$^{-1}$) as well.[18] After being etched with H$_2$O$_2$ for 30 s at 90°C, the intensity of the oxide peak was significantly increased, whereas the Ge peak was weakened. The etching mechanism of Ge by H$_2$O$_2$ can be explained using the following reactions:[19]

**Table 2.** BET specific surface areas of micrometer powder Ge and five types of asymmetric Ge membranes.

<table>
<thead>
<tr>
<th></th>
<th>CA Ge Mem</th>
<th>PAN Ge Mem</th>
<th>PAN Ge Mem 30 s</th>
<th>PAN Ge Mem 2 min</th>
<th>DC PAN Ge Mem 30 s</th>
<th>Micrometer powder Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area [m$^2$ g$^{-1}$]</td>
<td>15.28 ± 0.03</td>
<td>16.70 ± 0.02</td>
<td>42.55 ± 0.17</td>
<td>39.78 ± 0.14</td>
<td>91.15 ± 0.36</td>
<td>0.5830 ± 0.0037</td>
</tr>
</tbody>
</table>

**Figure 3.** SEM image and corresponding EDS mappings of DC PAN Ge Mem 30 s electrode after the long-term cyclability tests, as shown in Figure 6d. Scale bars: 10 μm.

**Figure 4.** a) Raman spectra and b) PXRD patterns of micrometer powder Ge and five types of Ge asymmetric membranes (* from oxidized Ge and + from elemental Ge).
2H₂O₂ → H₃O₂⁺ + O₂H⁻  \hspace{1cm} (1)

H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O  \hspace{1cm} (2)

Ge + O₂H⁻ + H₂O → Ge(OH)₂⁺ + OH⁻ + 2e⁻  \hspace{1cm} (3)

Ge(OH)₂⁺ + H₂O → H₂GeO₃ (aq) + 2H⁺  \hspace{1cm} (4)

Ge(OH)₂⁺ + 2OH⁻ → H₂GeO₃ (aq) + H₂O  \hspace{1cm} (5)

After 2 min of H₂O₂ etching, both Ge and GeO₂ peaks completely disappeared due to the loss of a significant amount of Ge from the membrane surface. This fact is also corroborated by TGA and PXRD data. Because DC PAN Ge Mem 30 s is coated with carbonaceous membranes, it is not surprising to observe much weaker Raman scatterings from Ge or GeO₂ compared with PAN Ge Mem 30 s because the penetration depth of Raman laser through condensed materials is limited to ≈50–100 nm.[20]

PXRD data of various asymmetric Ge membranes are shown in Figure 4b. The concentration of elemental Ge in PAN Ge Mem is much higher than that in CA Ge Mem. It is because polyacrylonitrile can better protect Ge from being oxidized during high-temperature carbonization with cellulose acetate propionate because it has a different molecular composition, that is, polyacrylonitrile is composed of C, H, and N, whereas cellulose acetate propionate contains C, H, and O atoms. After 30 s H₂O₂ etching at 90 °C, both Ge and GeO₂ patterns can be detected in the asymmetric membrane (PAN Ge Mem 30 s). After 2 min etching, only oxidized Ge patterns can be identified from the membrane (PAN Ge Mem 2 min). In contrast, PXRD patterns from elemental Ge in DC PAN Ge Mem 30 s are much stronger than those in PAN Ge Mem 30 s, probably due to the reduction of oxidized Ge in the unique sandwich-like structure during high-temperature carbonization.[21] Quantitative PXRD analyses indicate that the mass ratios of Ge to GeO₂ in DC PAN Ge Mem 30 s, PAN Ge Mem 30 s, and PAN Ge Mem 2 min are 52:48, 5:95, and 0:100, respectively. The oxidation states of Ge on the surface of DC PAN Ge Mem 30 s were identified using Ge (3d) XPS spectrum (Figure 5a). The strong peak centered at 33.0 eV can be assigned to oxidized Ge (+4), whereas the weak peak at 29.6 eV is attributed to elemental Ge.[22] C 1s peak at 284 eV matches well with C–C (sp² hybridized orbitals) and the binding energy of oxygen is close to the one from GeO₂ (Figure 5b,c).[23] The atomic ratio between C:Ge:O was determined to be 80.7:6.7:12.6, indicating that the surface is carbon rich and the outmost Ge layer has been mostly oxidized.

![Figure 5. XPS spectra of DC PAN Ge Mem 30 s: a) Ge (3d); b) C (1s); c) O (1s).](image-url)
The content of Ge in the asymmetric membranes was quantified by a TGA using compressed air as the purge gas (Table 3 and Figure S3, Supporting Information). The concentrations of Ge in CA Ge Mem and PAN Ge Mem were calculated to be 63.0% and 75.2%, respectively. After being etched at 90 °C for 30 s using ≈30 wt% hydrogen peroxide, 51.7 wt% Ge remained in PAN Ge Mem, implying that the extra void space has been generated to better accommodate the large volume expansion. DC PAN Ge Mem 30 s (40.2%) has 11.5% less Ge compared with PAN Ge Mem 30 s because the carbonaceous membrane coating does not contain Ge. Extended H₂O₂ etching can cause a significant loss in Ge, as evident by only 16.5% Ge left in PAN Ge Mem 2 min.

### Table 3. Thermogravimetric analyses of five types of asymmetric Ge membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O₂ etching time [s]</th>
<th>Ge content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA Ge Mem</td>
<td>0</td>
<td>63.0</td>
</tr>
<tr>
<td>PAN Ge Mem</td>
<td>0</td>
<td>75.2</td>
</tr>
<tr>
<td>PAN Ge Mem 30 s</td>
<td>30</td>
<td>51.7</td>
</tr>
<tr>
<td>PAN Ge Mem 2 min</td>
<td>120</td>
<td>16.5</td>
</tr>
<tr>
<td>DC PAN Ge Mem 30 s</td>
<td>30</td>
<td>40.2</td>
</tr>
</tbody>
</table>

3.3. Electrochemical Evaluation of Asymmetric Ge Membranes as LIB Anode

CA Ge Mem and PAN Ge Mem demonstrated outstanding delithiation capacities during the first formation cycles (1230 and 1130 mAh g⁻¹, respectively, at 50 mA g⁻¹; Figure S4, Supporting Information). When the current density was increased to 160 mA g⁻¹, the capacities were slightly reduced to ≈1100 and 950 mAh g⁻¹ (Figure 6a), which indicates that asymmetric Ge membranes have an excellent rate performance, due to the high electrical conductivity and fast lithium-ion diffusivity as mentioned previously.[10] However, CA Ge Mem and PAN Ge Mem did suffer from 73.6% and 75.5% capacity losses in 50 cycles at 160 mA g⁻¹ because Ge concentrations are very high (63.0 and 75.2 wt%, respectively), entailing a large electrode volume change that can cause serious electrode delamination and pulverization (Table 3 and Figure 6a). It is noteworthy that such cyclability is still much better than that of micrometer powder Ge control, whose capacity was eroded to less than 270 mAh g⁻¹ after two formation cycles and further reduced to less than 160 mAh g⁻¹ in as few as ten cycles at 160 mA g⁻¹ (Figure S4, Supporting Information), whose results are consistent with literature reports.[11,24]

To enhance the cycling stability of asymmetric Ge membranes as the LIB anode, we initially managed to etch CA Ge Mem using concentrated hydrogen peroxide solutions to generate an oxide

![Graph a) Cycling performance of five types of asymmetric Ge membranes; b) cycling performance and Coulombic efficiency of DC PAN Ge Mem 30 s; c) rate and cycling performance of PAN Ge Mem 30 s; d) rate and cycling performance of DC PAN Ge Mem 30 s.](image-url)
layer and extra void space to better accommodate the large volume change. But the membrane was relatively fragile and thus broken into pieces during H₂O₂ etching. PAN Ge Mem, in contrast, was robust enough to maintain the unique asymmetric porous structure after etching. It was reported that nanoscale Ge oxide has a much better cycling stability compared with bulk Ge because oxygen in Ge oxide can help reduce electrode volume expansion and form Li₂O passivation layer for an improved long-term cyclability.[9,25] The initial capacity of PAN Ge Mem etched by H₂O₂ at 90 °C for 30 s was 810 mA h g⁻¹, 83.7% of which can be retained after 50 cycles at 160 mA g⁻¹ (PAN Ge Mem 30 s, Figure 6a). The lower initial capacity of PAN Ge Mem 30 s can be attributed to the reduction in Ge content from 75.2 to 51.7 wt% due to etching (Table 3). The initial capacity loss (ICL) of PAN Ge Mem 30 s is higher than that of PAN Ge Mem (Table 4 and Figure S4, Supporting Information, 38.0% vs 12.2%) because there is a significant amount of GeO₂ in PAN Ge Mem 30 s, as confirmed by PXRD and Raman data. It is known that GeO₂ can react with lithium ions to produce electrochemically irreversible Li₂O, thereby leading to an increased ICL (Equation (6) and (7)).

\[ \text{GeO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Ge} + 2\text{Li}_2\text{O} \quad (6) \]

\[ 4\text{Ge} + 22\text{Li}^+ + 22\text{e}^- \leftrightarrow \text{Ge}_4\text{Li}_{22} \quad (7) \]

PAN Ge Mem 2 min (2 min H₂O₂ etching) electrode showed excellent capacity retention (92.6% in 50 cycles) due to the existence of a larger void space and an asymmetric porous structure (Figure S1, Supporting Information, Figure 2 and 6a). However, the capacity of PAN Ge Mem 2 min is quite low (430 mA h g⁻¹) because there is only 16.5% Ge (Table 3). Coating PAN Ge Mem 30 s with carbonaceous membranes (DC PAN Ge Mem 30 s) can significantly enhance the cyclability, as evidenced by more than 95% capacity retention at 160 mA g⁻¹ in 50 cycles (Figure 6a,b). Such an impressive cyclability is closely related to surface coating and a unique sandwich-like structure that can prevent the loss of surrounding Ge powders in DC PAN Ge Mem 30 s, as discussed previously. It is interesting to find out there is only a (nearly) singular peak around 0.44 V during the first oxidation sweep of DC PAN Ge Mem 30 s due to the oxidation of Ge into GeO₂, as discussed previously. It is interesting to find out there is only a (nearly) singular peak around 0.44 V during the first oxidation sweep of DC PAN Ge Mem 30 s due to the oxidation of Ge into GeO₂, as discussed previously. It is interesting to find out there is only a (nearly) singular peak around 0.44 V during the first oxidation sweep of DC PAN Ge Mem 30 s due to the oxidation of Ge into GeO₂, as discussed previously. It is interesting to find out there is only a (nearly) singular peak around 0.44 V during the first oxidation sweep of DC PAN Ge Mem 30 s due to the oxidation of Ge into GeO₂, as discussed previously. It is interesting to find out there is only a (nearly) singular peak around 0.44 V during the first oxidation sweep of DC PAN Ge Mem 30 s due to the oxidation of Ge into GeO₂, as discussed previously.
change in the SEI layer. The Nyquist plots of DC PAN Ge Mem 30 s shown in Figure 7c were also fitted using an equivalent circuit consisting of $R_s$, $R_{\text{ct}}$, $R_{\text{SEI}}$, and $W_d$. $R_s$ is electrolyte resistance, $R_{\text{ct}}$ is the charge transfer resistance of Ge powders, $R_{\text{SEI}}$ is the resistance from the SEI layer, constant phase element (CPE) is the capacitive resistance from the double layer, and $W_d$ stands for Warburg diffusion impedance (Figure 7d).[27] Figure 7d also shows the fitted values of $R_s$, $R_{\text{ct}}$, and $R_{\text{SEI}}$ resistances. In general, $R_s$ and $R_{\text{ct}}$ remained quite stable throughout the 170 cycles, whereas $R_{\text{SEI}}$ resistance was slightly increased from the initial 5.0 to 37.4 $\Omega$ at the 170th cycle. The increased $R_{\text{SEI}}$ is related to the inevitable breakdown of micrometer powder Ge which can cause the exposure of the new interface, hence consuming an extra amount of electrolyte to form a new SEI layer. Assuming that lithium-ion diffusion is the rate-limiting step, the diffusion coefficient of Li in DC PAN Ge Mem 30 s electrode was approximately calculated using the cyclic voltammetry data shown in Figure 7e,f and Randles–Sevcik equation below (Equation (8))[28]

$$I_p = (2.69 \times 10^2)n^{1.5}AD_{\text{Li}}^{0.5}C_{\text{Li}}^{0.5}$$

where $I_p$ is the cathodic peak current in amps due to lithium insertion, $n$ is the number of charges transferred, $A$ is the surface area of micrometer-size Ge particles in cm$^2$ that equals the product of
BET specific surface area (Table 2) and electrode mass, $C_{\text{Li}}$ is the bulk concentration of lithium ion in mol cm$^{-3}$, and $v$ is the scan rate in V s$^{-1}$. $D_{\text{Li}}$ represents the diffusion coefficient of Li in DC PAN Ge Mem 30 s electrode, which was calculated to be $1.9 \times 10^{-13}$ cm$^2$ s$^{-1}$. This value is close to the diffusivity of Li in the Ge thin film reported in the literature (1.5 $\times$ 10$^{-13}$ cm$^2$ s$^{-1}$).[29] The enhanced diffusion rate is probably due to the existence of abundant pores that resulted from phase inversion.[30] Notably, the reported experimental values of Li diffusion coefficients in silicon span four orders of magnitude from 10$^{-14}$ to 10$^{-10}$ cm$^2$ s$^{-1}$ because particle size, crystallinity, defect density, and experimental conditions may significantly affect the diffusion energy barrier.[30]

Finally, the cycled DC PAN Ge 30 s electrode (170 cycles totally, see Figure 6c) was opened, rinsed by DEC, and examined using SEM and EDS mapping. No apparent microcracks or fractures were observed on the membrane surface (Figure 3). This fact strongly suggests that the SEI layer is integral even after 170 times of repeated lithiation/delithiation, which is critical to long-term cyclability.

4. Conclusion

Various types of asymmetric Ge membranes have been synthesized to test the effects of polymer, H$_2$O$_2$ etching, and surface coating on electrode cyclability. Although the pristine asymmetric membrane structure can improve the cycling stability of Ge-based LIB anodes to a certain degree, the extremely large volume change requires hydrogen peroxide etching to generate extra void space and thus significantly increase the electrode cycle life. However, the etching process must be well controlled to avoid a significant loss of active materials, which can result in a very low capacity. Coating H$_2$O$_2$-etched Ge membrane with carbonaceous membranes can not only make the electrode more cyclable but also enhance the rate performance because of the unique sandwich-like porous structure and conversion of GeO$_2$ to elemental Ge through high-temperature carbon reduction. The gained knowledge can provide a beneficial guidance for the design of next-generation high-capability LIB anodes with large volume changes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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