



Co-axial fibrous silicon asymmetric membranes for high-capacity lithium-ion battery anode

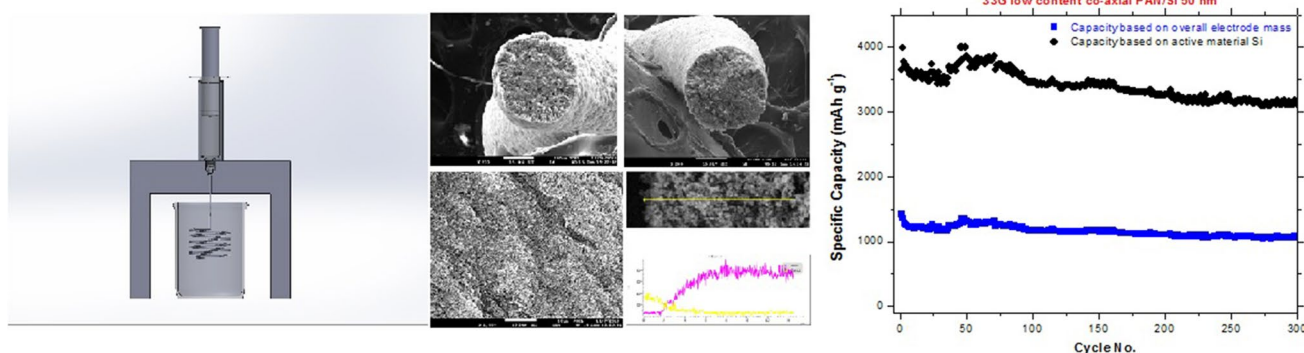
Ji Wu¹ · Christopher Anderson¹ · Parker Beaupre¹ · Shaowen Xu² · Congrui Jin³ · Anju Sharma⁴

Received: 27 March 2019 / Accepted: 31 July 2019 / Published online: 13 August 2019
© Springer Nature B.V. 2019

Abstract

Silicon as a promising candidate for the next-generation high-capacity lithium-ion battery anode is characterized by outstanding capacity, high abundance, low operational voltage, and environmental benignity. However, large volume changes during Si lithiation and de-lithiation can seriously impair its long-term cyclability. Although extensive research efforts have been made to improve the electrochemical performance of Si-based anodes, there is a lack of efficient fabrication methods that are low cost, scalable, and self-assembled. In this report, co-axial fibrous silicon asymmetric membrane has been synthesized using a scalable and straightforward phase inversion method combined with dip coating as inspired by the hollow fiber membrane technology that has been successfully commercialized over the last decades to provide billions of gallons of purified drinking water worldwide. We demonstrate that ~90% initial capacity of co-axial fibrous Si asymmetric membrane electrode can be maintained after 300 cycles applying a current density of 400 mA g⁻¹. The diameter of fibers, size of silicon particles, type of polymers, and exterior coating have been identified as critical factors that can influence the electrode stability, initial capacity, and rate performance. Much enhanced electrochemical performance can be harvested from a sample that has thinner fiber diameter, smaller silicon particle, lower silicon content, and porous carbon coating. This efficient and scalable approach to prepare high-capacity silicon-based anode with outstanding cyclability is fully compatible with industrial roll-to-roll processing technology, thus bearing a great potential for its future commercialization.

Graphic abstract



Keywords Silicon · Fibrous · Asymmetric membrane · Co-axial · Lithium-ion battery · Anode

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10800-019-01343-w>) contains supplementary material, which is available to authorized users.

✉ Ji Wu
jwu@georgiasouthern.edu

Extended author information available on the last page of the article

Abbreviations

LIBs	Lithium-ion batteries
NPs	Nanoparticles
Si	Silicon
SEM	Scanning electron microscope
EDS	Energy-dispersive X-ray spectroscopy
PXRD	Powder X-ray diffractometer

TGA	Thermogravimetric analyzer
BET	Brunauer–Emmett–Teller
XPS	X-ray photoelectron spectroscopy
PAN	Polyacrylonitrile
PS	Polysulfone
CB	Carbon black
NMP	<i>N</i> -methyl-2-pyrrolidone
EIS	Electrochemical impedance spectroscopy
G	Gauge
SEI	Solid electrolyte interphase
rpm	Rotations per minute

1 Introduction

Efficient energy storage devices with high energy and power density are much craved in the fields of portable electronics, electric vehicles, and intermittent power generation [1]. Although state-of-the-art commercial lithium-ion batteries (LIBs) have decent capacity, high reliability, and durability, they cannot fully meet the ever-increasing demand from the above-mentioned applications [2]. To further improve the potential of this dominating technology, revolutionary changes in electrode materials, binders, additives, and electrolytes are needed [3, 4]. Recently, silicon-based anode has attracted significant research attention due to its impressive theoretical capacity (3580 mAh g⁻¹ for Li₁₄Si₅ compared to 372 mAh g⁻¹ for commercial graphite anode), high abundance, environmental benignity, and low operational voltage [5, 6]. However, large volume changes during Si lithiation/de-lithiation can cause electrode delamination, detachment of active materials from conductive additives, unstable solid electrolyte interphase (SEI), thus resulting in rapid and permanent capacity loss [7]. Various nanostructures have been intensively explored to increase the cycling stability of Si-based anode, including nanoparticles (NPs), nanowires, nanorods, thin film, core-shell particles, porous silicon to Si/C composites, etc. [6, 8]. Specific binders and electrolyte additives also have beneficial effects on the stability of Si-based electrode [9, 10]. Most recently, 3-D nanostructures have demonstrated to be very efficient in stabilizing Si-based LIB anode [11–16]. However, significant challenges remain to prepare such 3-D nanostructures using a method that is efficient, low cost, scalable, and self-assembled [17].

Reverse osmosis asymmetric membranes can be reproducibly fabricated on a large scale via a roll-to-roll processing technology to provide billions of gallons of purified drinking water in the United States alone [18–20]. Thin film reverse osmosis asymmetric membranes have a nanoporous skin layer and a macroporous bottom layer [21]. This unique 3-D porous structure has been adopted by our research group for the first time to improve the cycling performance of various kinds of high-capacity LIB anodes to

some extent [22–24]. The macroporous layer can efficiently accommodate large volume changes of high-capacity alloying electrodes while the nanoporous layer can prohibit fractured active materials from falling away. However, fractured materials can be partially lost from the macroporous bottom layer [22, 25]. In addition, active materials on the surface of nanoporous layer may enter the electrolyte during repeated charging/discharging, thus contributing to certain capacity loss.

Being inspired by the hollow fiber membrane technology that has been successfully commercialized in the last decades to provide billions of gallons of purified drinking water worldwide, we synthesized various kinds of fibrous silicon (Si) asymmetric membranes via a simple phase inversion method combined with dip coating to solve the intrinsic problems associated with thin film reverse osmosis asymmetric membranes for high-capacity LIB anodes. It is because (1) the surface of fibrous Si asymmetric membrane consists of nanoporous skin layer only; and (2) coating fibrous silicon asymmetric membrane with nanoporous carbonaceous membrane that does not contain any silicon can further reduce the loss of active materials. The fibrous asymmetric membranes have been studied using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, powder X-ray diffractometer (PXRD), thermogravimetric analyzer (TGA), surface area analyzer (BET method), and X-ray photoelectron spectroscopy (XPS), as well as various electrochemical characterizations. Fiber diameter, Si particle size, Si concentration, type of polymer, and porous carbon coating have been identified as key factors that can influence the electrochemical performance of these membrane electrodes. Co-axial fibrous Si asymmetric membrane electrode demonstrates the most outstanding cycling and rate performance, e.g., ~90% initial capacity at ~1200 mAh g⁻¹ can be maintained in 300 cycles applying a current density of 400 mA g⁻¹.

2 Experimental section

2.1 Fabrication of fibrous Si asymmetric membranes using 21-gauge (G) needle

Firstly, 0.50 g polyacrylonitrile (PAN, $M_n \approx 150,000$, powders, Pfaltz & Bauer) or 1.0 g polysulfone (PS, $M_n \approx 60,000$, pellets, Acros), 0.15 g carbon black (CB, TIMCAL SUPER C45 with a surface area of 45 m² g⁻¹), 0.30 g silicon powder with a nominal average diameter of 50 nm (Alfa Aesar, laser synthesized, S1) or 100 nm (Alfa Aesar, plasma synthesized, S1), 10 mL of *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich, > 99.5%), and 10 pieces of zirconia mill balls were placed in a 100-mL zirconia mill jar. The jar was then mounted on a planetary ball mill (Across International,

PQ-N04 Planetary Ball Mill) and set to 50 rotations per minute (rpm) for 3 h to obtain a uniform slurry. Next, the slurry was transferred into a 10 mL syringe (Air-Tite Products Co.) equipped with a 21G needle (Air-Tite Products Co.). The slurry was extruded manually at a rate of $\sim 1 \text{ mL min}^{-1}$ into deionized water ($> 17 \text{ M}\Omega \text{ cm}$) to generate fibrous membranes via a so-called phase inversion mechanism [26, 27]. After being immersed in the water for 30 min, the fibers were collected, dried, and placed into an alumina combustion boat (5 mL, Sigma Aldrich). The boat was then loaded into a quartz tube that was treated at 800°C for 2 h using a Lindberg/Blue M™ 1100 $^\circ\text{C}$ tube furnace with a ramp rate of $\sim 60^\circ\text{C min}^{-1}$ to yield carbonized, conductive fibrous Si membranes for LIB anodes. The boat was protected by 200 sccm helium gas (99.9999%, Airgas He UHP300) during the treatment to avoid oxidation. Two kinds of asymmetric membranes were prepared using this method, which are labeled (1) *21G high content PS/Si 100 nm* and (2) *21G high content PAN/Si 100 nm*. 21G and PS represent the size of needle and the type of polymer, respectively. Si 100 nm stands for the nominal Si particle size. Four other fibrous asymmetric membranes that contain lower Si content were prepared using the same procedure except that the slurry is composed of 0.50 g PAN or 1.0 g PS, 0.25 g CB and 0.20 g Si powders dispersed in 10 mL NMP. They are labeled as (1) *21G low content PS/Si 100 nm*; (2) *21G low content PAN/Si 100 nm*; (3) *21G low content PS/Si 50 nm*; and (4) *21G low content PAN/Si 50 nm*.

2.2 Fabrication of fibrous Si asymmetric membranes using 33-gauge (G) needle

Electrochemical performance of fibrous Si asymmetric membranes fabricated using 21G needle is quite inferior, mainly because the fibers are so thick that lithium-ion diffusion is significantly hindered. To reduce fiber diameter, we tried to manually extrude the same slurry (0.50 g PAN, 0.25 g CB, and 0.20 g Si powders dispersed in 10 mL NMP) using a smaller needle, e.g., 33 G (Air-Tite Products Co. TSK STERIJECT). However, we failed to do so because of the huge resistance coming from the viscous slurry. Therefore, a special homebuilt device was fabricated to assist the extrusion process as shown in Figs. 1 and S2. One-ton manual arbor press was utilized to create enough compress load to eject highly viscous solution into deionized water to form fibrous membranes. The extrusion speed was controlled at $\sim 1 \text{ mL min}^{-1}$. Low-cost disposable plastic syringes instead of expensive stainless-steel ones were used in this study. To avoid the deformation of the plastic syringe under the high-pressure loading condition, a cylindrical metal barrel jacket was built to mechanically support the plastic barrel (S2). Metal block with a central hole was employed to prevent leakage at the junction between the needle adapter and the syringe barrel during the high-pressure extrusion process (S2). In addition, plastic plunger was replaced by reusable house-made metal plunger to avoid bending and distortion. The as-prepared fibers were carbonized at 800°C for 2 h and

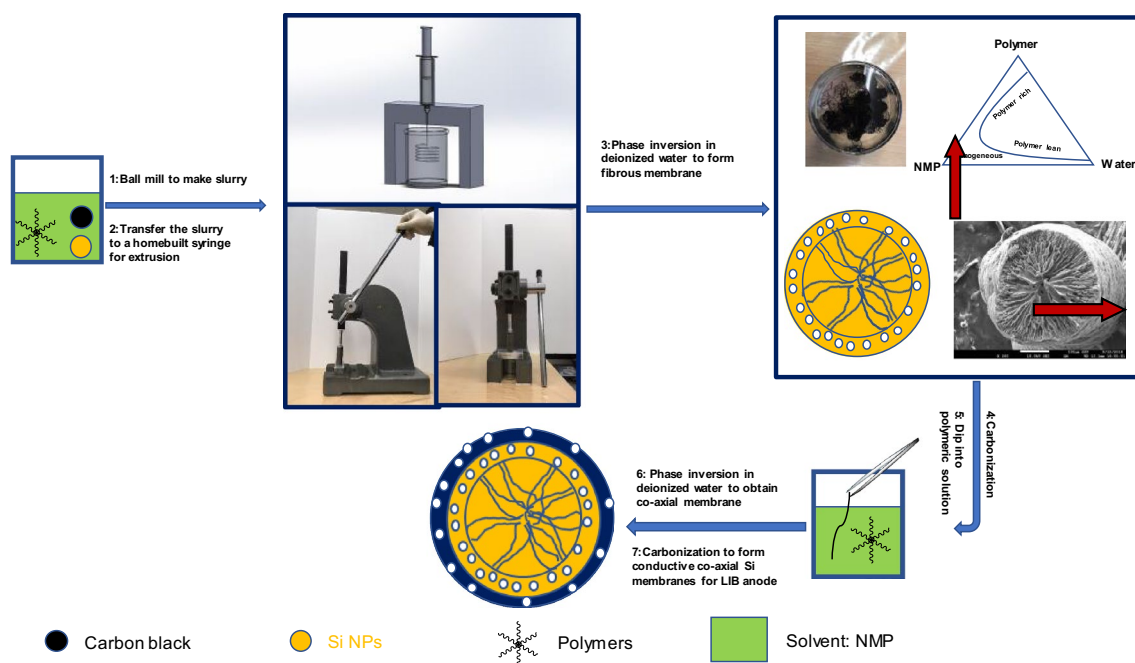


Fig. 1 Illustrative diagram showing the fabrication process to obtain co-axial fibrous Si asymmetric membranes for high-capacity lithium-ion battery anode

labeled as *33G low content PAN/Si 50 nm*. Illustrative diagram and photo images of the homebuilt device are shown in Figs. 1 and S2, respectively.

2.3 Fabrication of 33G co-axial fibrous Si asymmetric membranes using a dip-coating method

33G low content PAN/Si 50 nm fiber was dipped into a polymeric solution that contains 5.0 w/v% PAN in NMP using a pair of plastic tweezers. Next, the fiber was slowly pulled out from the polymeric solution to make a uniform coating that does not contain any silicon. Lastly, the coated fiber was treated in a tube furnace at 800 °C for 30 min and labeled as *33G low content co-axial PAN/Si 50 nm* in this study.

2.4 Fabrication of fibrous carbon asymmetric membranes using 33-gauge (G) needle

Fibrous carbon asymmetric membrane that does not contain any silicon was fabricated using the same method as that of *33G low content PAN/Si 50 nm*, except that the slurry does not contain silicon particles (0.50 g PAN and 0.25 g CB dispersed in 10 mL NMP). The membrane is labeled as *33G PAN/CB* and used as a control (S3).

2.5 Characterization of fibrous Si asymmetric membranes

A field-emission scanning electron microscope (JEOL JSM-7600F) attached with a transmission electron detector was employed for the morphological and structural characterization. Elemental compositions of fibrous membranes were analyzed using an electron-dispersive X-ray spectroscopy (EDS) attached to the SEM. The specific surface areas of fibrous membranes were measured using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer and Brunauer–Emmett–Teller (BET) calculation method. All samples were degassed at 50 μ Torr and 300 °C for 30 min before the surface area measurement. The concentration of Si in fibrous membranes was quantified using a thermogravimetric analyzer (TA Instruments Q50 TGA) that was purged using high-purity compressed air gas (Ultra Zero, Airgas) at a flow rate of 20 mL min⁻¹. The oven temperature was first ramped to 120 °C and held for 10 min. Then it was increased to 700 °C at a rate of 10 °C min⁻¹ and held for 30 min.

A Thermo Scientific DXR SmartRaman Spectrometer was operated using a 532 nm laser of 1–3 mW, an objective lens of $\times 10$, a hole aperture size of 25 μ m, and a total exposure time of 300 s. Powder X-ray diffraction (PANalytical Empyrean) was carried out using a Cu K α radiation ($\lambda = 1.542$ Å) from 10 to 90° (two theta) with a step rate of 0.1°/s. All samples were scanned for 32 times to improve

signal-to-noise ratio. The acceleration voltage and current were 40 kV and 40 mA, respectively. The oxidation states of silicon particles in 33G fibrous Si membranes were analyzed using an X-ray photoelectron spectroscopy (PHI 5000 Versaprobe XPS system from Physical Electronics, Inc.), which employed monochromatic Al K α X-rays of energy 1486.6 eV and 45° takeoff angle. Survey scans at a pass energy of 117.4 eV were performed for the chemical elemental identification while the pass energy for region scans is 23.5 eV to determine Si oxidation states. X-ray spot size of 200 μ m was used for all the samples.

2.6 Electrochemical evaluation of fibrous Si asymmetric membranes as LIB anodes

Electrodes were prepared by gluing fibrous membranes directly onto copper discs (15 mm in diameter and 11 μ m thick from MTI Corporation). The glue is made of 0.10 g carbon black and 0.16 g sodium carboxymethyl cellulose (Acros, $M_w = \sim 90,000$) that were uniformly dispersed in 3 mL deionized water through 3-h ball milling at 50 rpm. The uncalendered electrode was then dried at 100 °C for at least 4 h to remove residual water. The final mass loading per electrode is ~ 1.0 mg. The electrodes were assembled into 2032-type coin cells inside an argon-filled glove box using lithium metal (EQ-Lib-LiC25, MTI Corporation) as the counter electrode and 60 μ L 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. The concentration of oxygen and water inside the glove box (LCPW, LC Technology Solutions, INC.) is below 1 ppm. The membrane separator is made of polyethylene/polypropylene blend (MTI Corporation). Galvanostatic cycling tests of LIB half-cells were conducted using a multi-channel Potentiostat/EIS (BIO-LOGIC VMP3) at room temperature. The cells were charged and discharged at the same current density from 0.01 to 2.00 V (vs. Li/Li⁺). Two formation cycles at 50 mA g⁻¹ were performed before subsequent tests. Voltage was scanned periodically between 10 mV and 2.00 V during the cyclic voltammetry tests. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.1 Hz–1 MHz with 10 mV AC perturbation in fully delithiated state.

3 Results and discussion

3.1 Fabrication of fibrous Si asymmetric membranes

Thick fibrous Si asymmetric membranes can be simply prepared by pushing the slurry in a plastic syringe through a 21G

needle into deionized water, in which the slurry experiences phase separations to form asymmetric porous structure. NMP (solvent) in the slurry is de-mixed from polymer and mixed with water (non-solvent) to form one phase; whereas polymer (PAN or PS), CB, and Si NPs in the slurry precipitate to form another phase (Fig. 1). As a result, 3-D asymmetric porous structure with nanoporous skin and macroporous core can be naturally formed (Figs. 2, S3 and S4). The porosity and pore morphology can be tuned by varying the kind of solvent and no-solvent, type of polymer, polymer concentration, etc. [23, 28]. CB is used as a filler to maintain the asymmetric porous structure during high-temperature treatments, which can also increase the matrix conductivity [24, 29]. However, electrochemical performance of 21G fibrous Si asymmetric membranes is generally inferior mainly because the fibers are so thick ($\sim 400\ \mu\text{m}$, Figs. 2a–f, 6) that lithium-ion diffusion can be significantly hindered [30]. To reduce the thickness of fibrous membrane and thus enhance its electrochemical performance, a homebuilt extrusion system has been created to facilitate the ejection of viscous slurry under high pressure through a much smaller needle, e.g., 33G (Figs. 1, S2). It is noteworthy that such a method is highly scalable as evident by forming $\sim 30\text{-m}$ -long continuous fibers per minute under our experimental conditions (S2). Equipped with needle arrays, yield could be further increased by orders of magnitude.

The porosity of co-axial fibrous silicon asymmetric membrane was calculated to be ~ 0.70 using the following formula:

$$\text{Porosity} = 1 - \frac{\text{Nominal density}}{\text{Theoretical density}},$$

where theoretical density is equal to the density of silicon times its mass percentage plus the density of carbon times its mass percentage ($d_{\text{Si}} \times \text{wt}\%_{\text{Si}} + d_{\text{C}} \times \text{wt}\%_{\text{C}}$), and nominal density is equal to the mass of co-axial fibrous silicon asymmetric membrane divided by its volume ($\frac{\text{Mass of co-axial fibrous Si}}{\pi r^2 L}$; r is the radius of Si fiber; L is the length of Si fiber). Such a high porosity is necessary and beneficial for Si-based LIB anodes because the volume change of silicon is as large as $\sim 400\%$ during lithiation and de-lithiation [8].

It is also notable that the mass ratio of silicon to carbon can be well controlled by tuning the composition of the slurry made of PAN, CB, and Si. After the carbonization, the mass ratio of silicon to carbon is very close to our theoretical calculation using the following formula:

$$\frac{\text{Mass}_{\text{Silicon}}}{\text{Mass}_{\text{Carbon}}} = \frac{\text{Mass}_{\text{Silicon}}}{\text{Mass}_{\text{Carbon black}} + \text{Mass}_{\text{Polyacrylonitrile}} \times \left(\frac{3 \times 12}{3 \times 12 + 14} \right)}$$

Since the linear formula of PAN is $(\text{C}_3\text{H}_3\text{N})_n$, $\left(\frac{3 \times 12}{3 \times 12 + 14} \right)$ represents the mass percentage of carbon in PAN.

As shown in Fig. 2g, the diameter of fibrous Si asymmetric membrane can be significantly reduced to $\sim 220\ \mu\text{m}$ using our homebuilt extrusion system. By coating the surface of 33G fibrous Si asymmetric membrane with a thin layer of carbonaceous membrane ($\sim 2\ \mu\text{m}$ thick) that does not contain any Si particles, excellent cyclability can be obtained, i.e., $\sim 90\%$ initial capacity can be retained even after 300 cycles at $400\ \text{mA g}^{-1}$ (Figs. 2h–j, 6).

3.2 Characterization of fibrous Si asymmetric membranes

SEM images reveal that the type of polymer, Si concentration, and Si particle size can influence the porosity and pore morphology (Fig. 2). In general, fibrous membranes made from PS have larger finger-like pores and higher porosities as compared to the fibers made from PAN. It is well known that the type of polymer has a drastic impact on phase separation kinetics (de-mixing process) and thereby result in a huge difference in porosity and pore morphology, which phenomenon has been well studied by membrane society [31, 32]. The quicker de-mixing kinetics in PS solution leads to the formation of larger finger-like voids [32–34]. Higher Si content and smaller Si particle can decrease membrane porosity and pore size (Fig. 2) because smaller Si particles may easily infiltrate into finger-like pores and thereby reduce the porosity and pore size. Such an argument is also corroborated by the fact that PAN/CB fibrous asymmetric membrane that does not contain Si particles are much more porous compared to PAN/Si membranes (S3 vs. Fig. 2g). Elemental mapping and EDS line scan (S4) confirm that silicon is uniformly distributed throughout the porous, carbonaceous matrix in fibrous membranes, thus benefiting uniform electrode expansion and structural stability.

Si concentration in fibrous membranes can be quantified using a thermogravimetric analyzer that utilizes compressed air as the purging gas (Table 1 and S5; Si: 27–44 wt%) [22]. High content PS/Si 100 nm membrane has relatively low content of silicon compared to high content PAN/Si 100 nm membrane because the concentration of PAN in the slurry is only 5% while the concentration of PS is 10%. Notably, 5% PS solution tends to form droplets instead of fibrous membranes because it is not viscous enough. Low content PAN/Si 100 nm membrane has a lower Si concentration compared to high content PAN/Si 100 nm because their slurries have different CB:Si ratios (see experimental section). Carbon concentration in 33G low content co-axial PAN/Si 50 nm asymmetric membrane is slightly higher than that of 33G low content PAN/Si 50 nm membrane because the coating is composed of pure carbon without silicon (Figs. 2j and S4). Specific surface areas of different kinds of fibrous Si membranes are listed in Table 2. Carbonized membranes

Fig. 2 Scanning electron microscope images of **a** 21G high content PS/Si 100 nm; **b** 21G high content PAN/Si 100 nm; **c** 21G low content PS/Si 100 nm; **d** 21G low content PAN/Si 100 nm; **e** 21G low content PS/Si 50 nm; **f** 21G low content PAN/Si 50 nm; **g** 33G low content PAN/Si 50 nm, **h** 33G low content co-axial PAN/Si 50 nm; **i** nanoporous surface of 33G low content co-axial PAN/Si 50 nm; and **j** cross-sectional EDS line scan of 33G low content co-axial PAN/Si 50 nm fibrous asymmetric membrane, indicating the presence of ~2- μ m-thick porous carbon coating on the core of fibrous Si asymmetric membrane

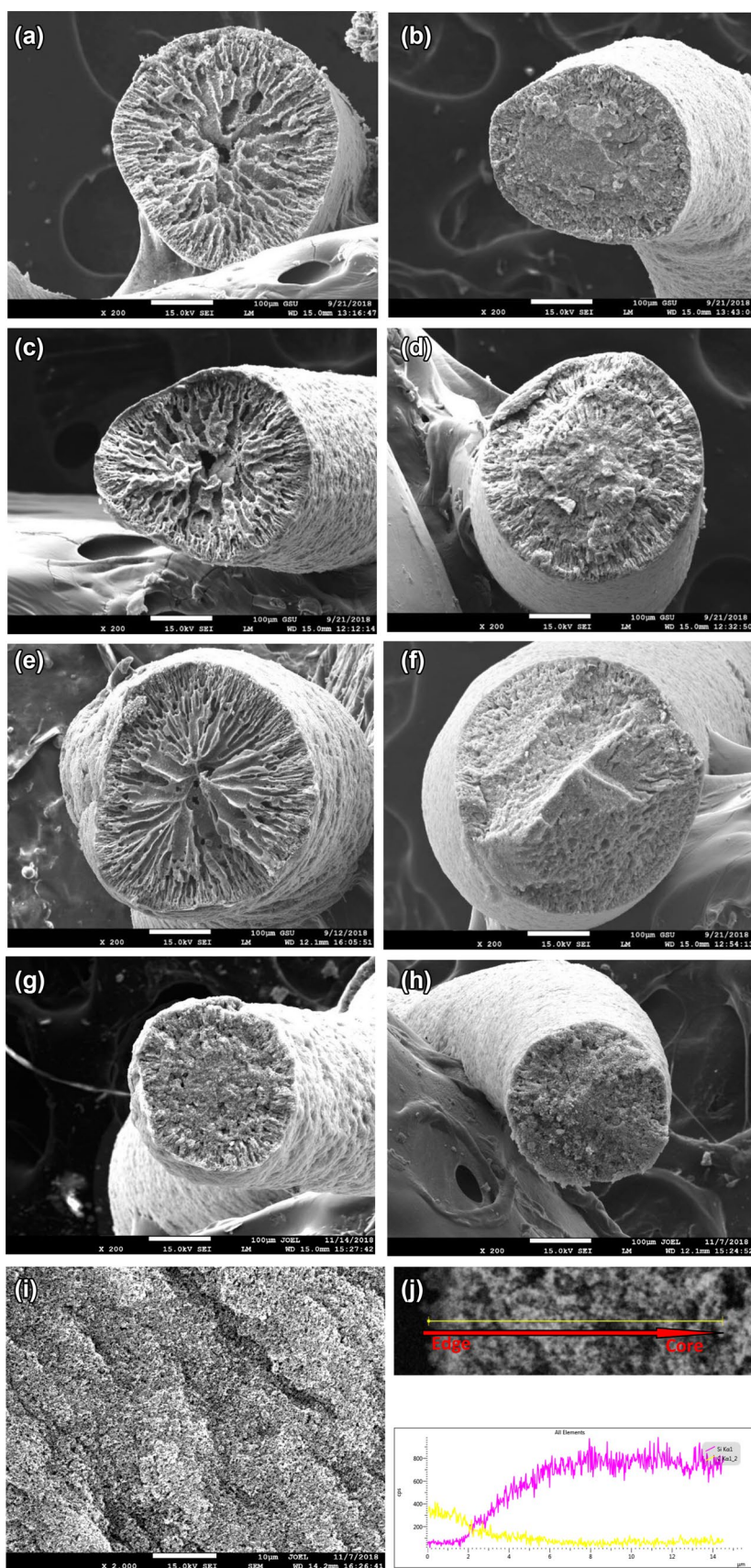


Table 1 Concentration of silicon and carbon in various types of fibrous Si asymmetric membranes

	21G high content PS/Si 100 nm	21G high content PAN/Si 100 nm	21G low content PS/Si 100 nm	21G low content PAN/Si 100 nm	21G low content PS/Si 50 nm	21G low content PAN/Si 50 nm	33G low content PAN/Si 50 nm	33G low content co-axial PAN/Si 50 nm
Si wt%	35	44	27	33	28	35	39	34
C wt%	65	56	73	67	72	65	61	66

made from PAN have much lower specific surface areas compared to the ones made from PS, which in fact is consistent with SEM data (Fig. 2). Smaller Si (50 vs. 100 nm) particles can easily infiltrate into carbonaceous porous structure and thus reduce specific surface area (Fig. 2, Table 2). The specific surface area of 33G low content co-axial PAN/Si 50 nm membrane ($\sim 86 \text{ m}^2 \text{ g}^{-1}$) is larger than that of 33G low content PAN/Si 50 nm membrane ($56 \text{ m}^2 \text{ g}^{-1}$) because the highly porous carbonaceous membrane on the top surface does not contain any Si nanoparticles which may block the pores and reduce the surface area (Table 2, S3, S4, and S6). Although the specific surface area of membranes made from PS is relatively high, the membranes are too fragile to survive the dip-coating process.

Raman spectra of various fibrous Si asymmetric membranes are shown in Fig. 3. The peak centered around 520 cm^{-1} can be attributed to Si NPs while carbon G and D peaks are located at ~ 1600 and 1350 cm^{-1} , respectively [35, 36]. Powder X-ray diffraction data confirm the presence of crystalline silicon in all kinds of fibrous Si asymmetric membranes as evident by three intense peaks at 28.34° , 47.27° , and 56.06° (Fig. 4). The three intense peaks correspond to the diffractions from crystal planes of Si (111), (220), and (311), respectively (JCPDS No. 27-1402) [37]. There is also a small sharp peak around 26.5° for 33G low content PAN/Si 50 nm, 33G low content co-axial PAN/Si 50 nm, and 33G PAN/CB membranes, which can be assigned to graphitic materials [38]. The same peak does not show up for other samples because PAN is relatively easier to form crystalline carbon after being treated at high temperatures as compared to PS [39]. In addition, lower concentration of silicon (impurity) can benefit the formation of crystalline carbon [40, 41]. The oxidation states of Si in 33G low content PAN/Si 50 nm and 33G low content co-axial PAN/Si 50 nm membranes are identified using Si(2p) XPS spectra shown in Fig. 5a while their C (1 s) spectra are provided in Fig. 5b. The peaks centered at 99.2 and 103.2 eV can be assigned to elemental Si (0) and oxidized silicon (IV), respectively [42]. The peak ratio between Si (0) and Si(IV) does not change significantly before and after the coating ($\sim 1:1$), indicating silicon NPs are chemically stable under our processing conditions, i.e., neither oxidized nor reduced significantly during the coating and following carbonization process. The mass ratios of Si to C were calculated to be 25:75 and 26:74 for 33G low

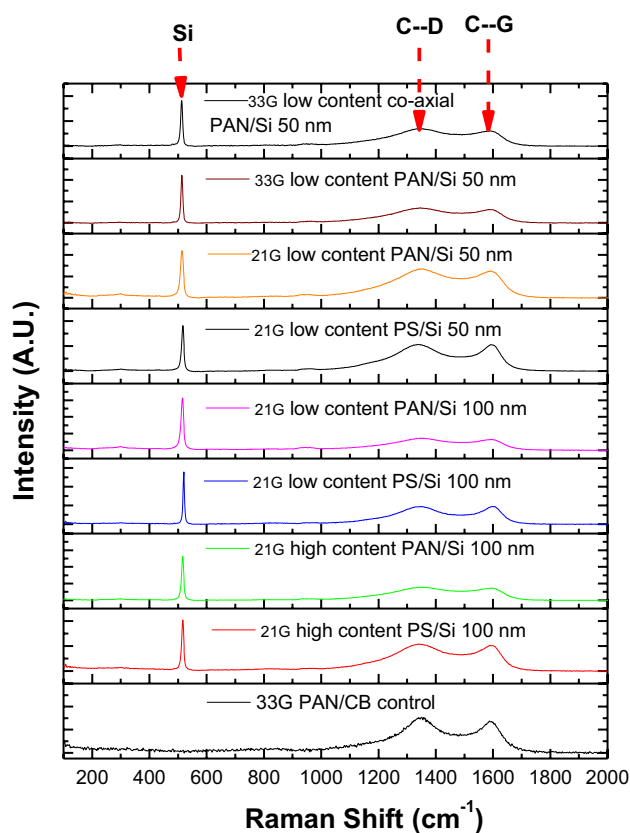
content PAN/Si 50 nm and 33G low content co-axial PAN/Si 50 nm membranes, respectively. Since XPS is a surface analytical instrument with a limited penetration depth, the mass ratios are quite different from the ones obtained from thermogravimetric analysis shown in Table 1. The lower Si-to-C mass ratios calculated from XPS data imply that silicon nanoparticles are surface coated with carbon thin film, thereby benefiting the formation of stable solid electrolyte interphase [43].

3.3 Electrochemical properties of fibrous Si asymmetric membranes as LIB anodes

33G low content co-axial PAN/Si 50 nm fibrous asymmetric membrane demonstrates the most outstanding electrochemical performance among eight types of membranes that are different in Si particle size, Si concentration, type of polymer, fiber thickness, and carbonaceous coating as shown in Fig. 6. The initial capacity loss of co-axial fibrous membrane electrode calculated from the first formation cycle is only $\sim 14\%$ (see S7), implying that the unique structure can well withstand the large volume changes of active material, Si without significant electrode delamination and pulverization. The first de-lithiation capacity at a current density of 400 mA g^{-1} is as high as 1420 mAh g^{-1} or 20.5 mAh cm^{-2} (Fig. 6a). This capacity is based on the overall electrode mass including both silicon and carbon. After deducting the contribution from carbon ($\sim 66 \text{ wt}\%$, $\sim 280 \text{ mAh g}^{-1}$ at 400 mA g^{-1} ; Table 1 and Fig. 6c), the specific capacity of Si in 33G co-axial fibrous asymmetric membrane was calculated to be 3650 mAh g^{-1} which is very close to its theoretical capacity. The capacity drops to 1200 mAh g^{-1} or 17.3 mAh cm^{-2} in ten cycles and then remains highly stable until the end of cycling test with $\sim 90\%$ capacity retention (10th vs. 300th; Fig. 6a). The initial capacity drop is probably due to the formation of SEI layer and fracturing of large particles from commercial Si. When the current density is increased from 50 to 800 mA g^{-1} , the capacity is reduced by $\sim 40\%$, which is still remarkable considering that the fiber is thicker than $200 \mu\text{m}$ (Figs. 2h, 6b). 100th, 200th, and 300th cycles of co-axial fibrous membrane electrode have quite similar lithiation and de-lithiation voltage profiles (Fig. 6d), implying that a stable SEI layer has been formed and the unique porous structure is integral during the cycling test. The de-lithiation overpotentials for 5th

Table 2 BET (Brunauer, Emmett, and Teller) specific surface areas of various fibrous Si asymmetric membranes

	21G high content PS/Si 100 nm	21G high content PAN/Si 100 nm	21G low content PS/Si 100 nm	21G low content PAN/Si 100 nm	21G low content PS/Si 50 nm	21G low content PAN/Si 50 nm	33G low content PAN/Si 50 nm	33G low content co- axial PAN/Si 50 nm
Specific area ($\text{m}^2 \text{g}^{-1}$)	249.7 $\pm$ 6.8	106.2 $\pm$ 3.1	293.8 $\pm$ 7.9	72.2 $\pm$ 1.6	234.5 $\pm$ 6.1	60.1 $\pm$ 0.9	55.9 $\pm$ 0.2	86.4 $\pm$ 0.4

**Fig. 3** Raman spectra of various fibrous Si asymmetric membranes and 33G PAN/CB membrane control

and 10th cycles are slightly higher than other cycles because a stable SEI layer has not been fully developed yet. It is believed that such an excellent electrochemical performance originates from the unique structure of co-axial Si fibrous membrane. Firstly, the macroporous core can efficiently accommodate the large volume expansion of silicon during its alloying with lithium. Secondly, the nanoporous skin can prohibit the fractured silicon particles from falling off the electrode to certain degree. Thirdly, the co-axial carbon coating can not only further reduce the loss of fractured Si particles but also benefit the formation of stable SEI layer. Additionally, the carbonaceous co-axial coating is electrically conductive and highly porous, thus facilitating efficient transport of both electrons and lithium ions.

The cyclability of control sample, 33G PAN/CB is also outstanding as evident by no apparent capacity loss in 100 cycles (Fig. 6c). However, its specific capacity is quite low, i.e., $\sim 280 \text{ mAh g}^{-1}$ at 400 mA g^{-1} because it is made of carbon only. Fibrous membrane thickness has been identified as the most dominating factor that can impact both initial capacity and cycling stability, dwarfing other factors such as the size of Si particle, type of polymer, concentration of Si. All fibers fabricated using 21G needle are characterized

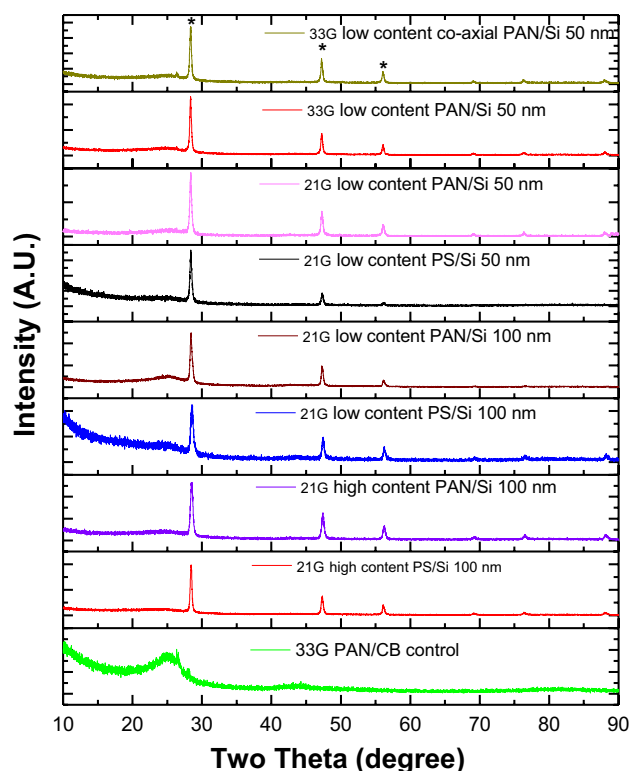


Fig. 4 Powder X-ray diffraction patterns of various fibrous Si asymmetric membranes and 33G PAN/CB membrane control (* represents the peaks from Si NPs)

by both low capacity and poor cyclability mainly due to its large thickness ($\sim 400\ \mu\text{m}$, Figs. 2, 6c). However, the fibers made from PAN do have much higher initial capacity than those made from PS because PAN tends to form more crystalline graphitic materials after being carbonized, thus

being more electrically conductive and mechanically robust [40, 44]. Reducing the concentration of Si in fibrous membranes can improve its cycling stability to certain degree but not dramatically because lower Si content corresponds to smaller electrode volume expansion. The size of Si particles also has certain effect on the cyclability and initial capacity. For instance, 21G low content PAN/Si 50 nm has a higher initial capacity than that of 21G low content PAN/Si 100 nm because the use of smaller Si particles can shorten lithium-ion diffusion length. It is well known that Si has a very low lithium-ion diffusion coefficient compared to commercial graphite anode (D_{Li^+} in bulk Si: $\sim 3 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$; D_{Li^+} in 50 nm Si: $\sim 5 \times 10^{-12}\ \text{cm}^2\ \text{s}^{-1}$) [45]. The diffusion coefficient of lithium in 50 nm Si was calculated using its geometric area instead of the real contact area, resulting in a greater-than-real diffusivity as acknowledged by Chen and Lieberwirth et al. [45]. Furthermore, smaller Si particles are mechanically more robust as revealed by in situ TEM observations, thereby leading to an improved cyclability [46]. The fibrous membrane made using a smaller needle, 33G low content PAN/Si 50 nm has a much enhanced cycling stability compared to 21G low content PAN/Si 50 nm, 86% of whose initial capacity can be retained in 100 cycles (Fig. 6c). It was reported that very thick electrodes suffer from gigantic ionic and electrical resistance, as well as large electrode volume change, thus causing inferior electrochemical performance in general [47, 48]. In our case, fibrous membranes fabricated using 21G needle ($\sim 400\ \mu\text{m}$) are nearly twice as thick as that of membranes prepared using 33G needle ($\sim 220\ \mu\text{m}$), which is the leading cause for the poor electrochemical performance of 21G fibrous membrane electrodes.

33G low content co-axial PAN/Si 50 nm fibrous asymmetric membrane electrode was also studied using cyclic voltammetry shown in Fig. 7a. Open circuit potential is scanned

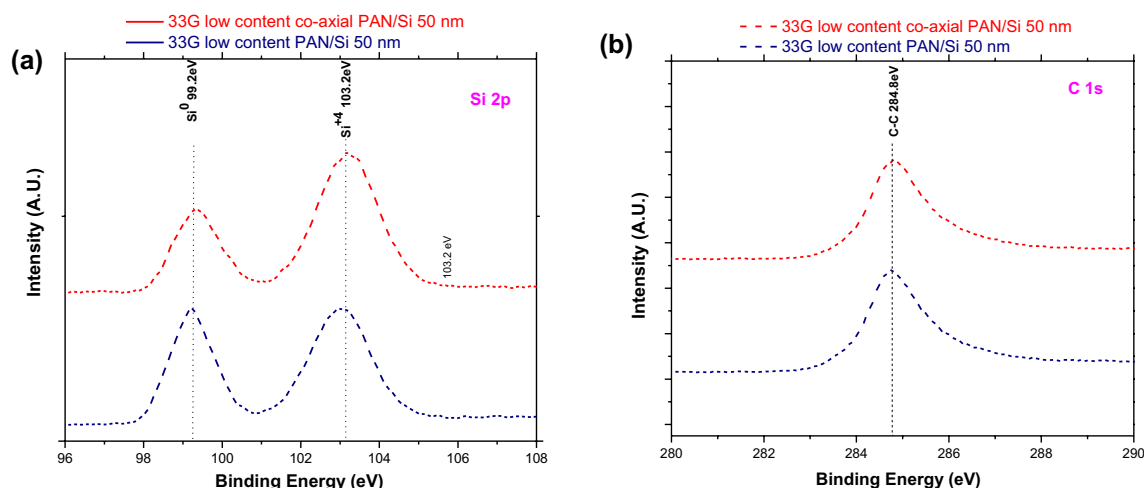


Fig. 5 X-ray photoelectron **a** Si 2p and **b** C 1s spectra of 33G low content PAN/Si 50 nm and 33G low content co-axial PAN/Si 50 nm fibrous asymmetric membranes

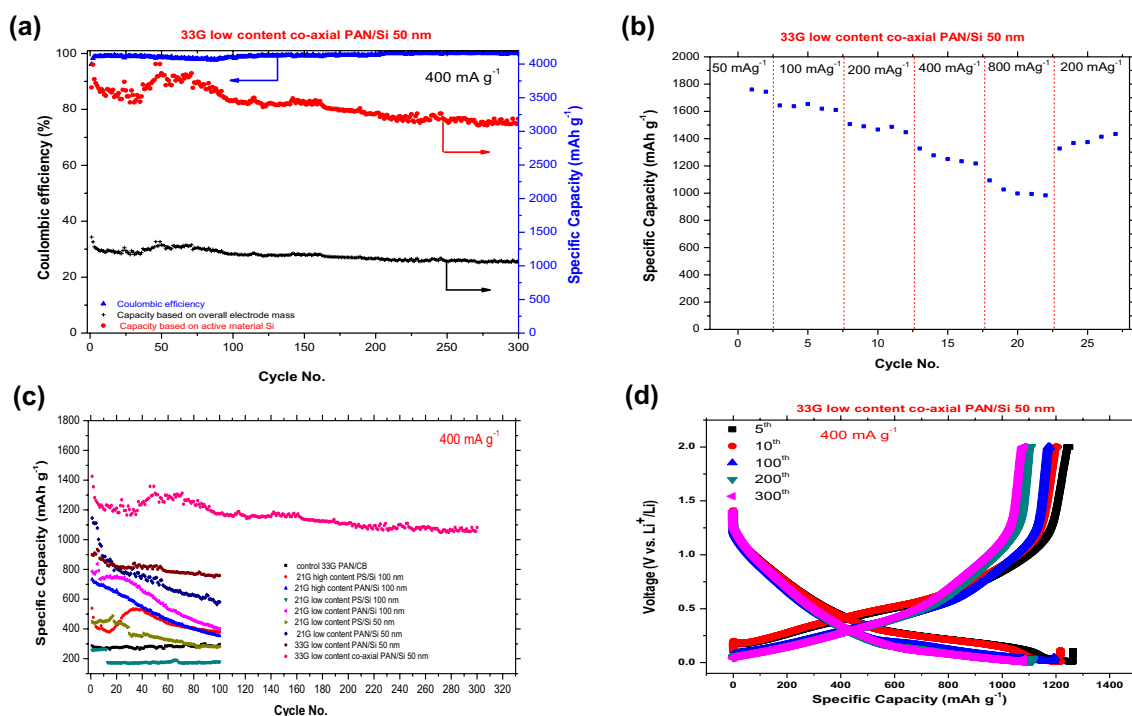


Fig. 6 Electrochemical characterization of various fibrous Si asymmetric membranes: **a** cycling test, **b** rate performance, and **d** voltage profiles of 33G low content co-axial PAN/Si 50 nm; **c** comparison of cyclability of different kinds of fibrous Si asymmetric membranes

periodically down to 0.01 V and then back to 2.00 V using 5 different rates (0.1, 0.2, 0.4, 0.8, and 1.6 mV/s in sequence). The broad cathodic peak ranging from 0.5 to 0.75 V in the 1st cycle using a scan rate of 0.1 mV s⁻¹ can be ascribed to electrolyte decomposition on the surface of membrane electrode [29]. However, the intensity of the broad peak drastically decreases in the subsequent cycles (2nd to 5th) at the same scan rate, implying that SEI layer can be rapidly stabilized in the unique co-axial fibrous membrane electrode. Another cathodic peak at ~0.1 V in the 1st cycle relates to the lithiation of crystalline silicon [37]. Two broad anodic peaks centered at ~0.35 and 0.55 V can be attributed to the de-lithiation of non-crystalline Si–Li alloy. It was reported that the lithiation process can cause amorphization of Si–Li alloy, which in turn lowers overpotential and enhance anodic currents in the subsequent cycles [49–51]. For example, the 0.1 V cathodic peak in the 1st cycle is shifted to ~0.2 V in the subsequent scans at 0.1 mV/s, indicating that overpotential is reduced after Si being amorphized. When the scan rate is increased from 0.1 to 1.6 mV/s, overpotentials for both lithiation and de-lithiation have been elevated, i.e., Si lithiation peak is decreased from 0.2 to 0.05 V while Si alloy de-lithiation peak is increased from 0.55 to 0.75 V. This fact is consistent with our rate test results (Fig. 6b) and related to the intrinsically low diffusion coefficient of lithium ions in Si as mentioned above. Assuming interfacial charge transfer is rapid and lithium diffusion is the rate limiting process, the

diffusion coefficient of Li in co-axial PAN/Si 50 nm fibrous membrane electrode can be roughly estimated using the data shown in Fig. 7b and Randles–Sevcik equation as shown below:

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li}^{0.5} C_{Li} \nu^{0.5} \quad (1)$$

where I_p is the cathodic peak current in amps corresponding to lithium insertion, n is the number of charges transferred, A is the surface area of 50 nm Si particles (25.3 m² g⁻¹ [52]) in cm² that is equal to the product of BET surface area and electrode mass, C_{Li} is the bulk concentration of lithium in mol cm⁻³, and ν represents CV scan rate in V s⁻¹. D_{Li} in co-axial PAN/Si 50 nm electrode was calculated to be 16.9×10^{-13} cm² s⁻¹ that is close to literature reported value as mentioned above [45, 53].

EIS spectra of fully de-lithiated (2.0 V) 33G low content co-axial PAN/Si 50 nm fibrous asymmetric membrane electrode at different cycles are shown in Fig. 7c. Ohmic internal resistance remains almost unchanged during the cycling test, implying that there is a good adhesion between fibrous membrane and copper current collector, and the fibrous membrane can efficiently accommodate the large volume expansion of silicon particles without significant electrode delamination. EIS spectra of the membrane electrode at 100th, 200th, and 300th cycles are very similar to each other, indicating the formation of integral and stable

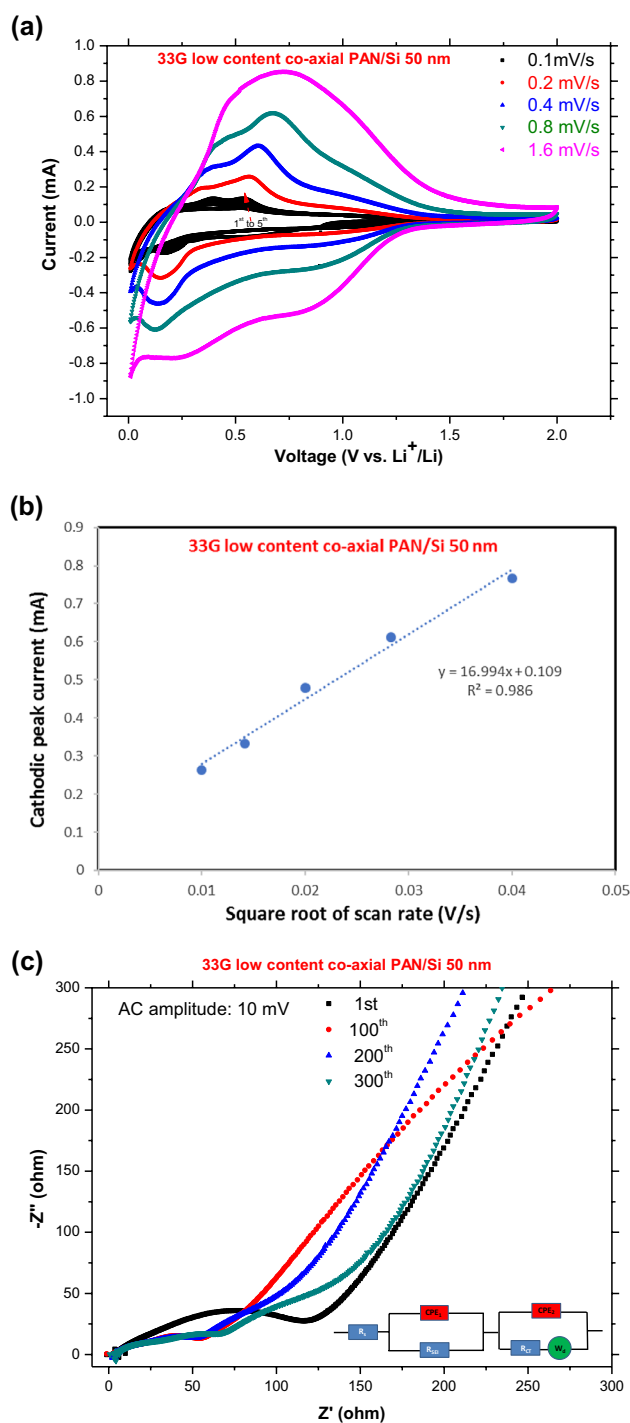


Fig. 7 **a** Cyclic voltammograms; **b** cathodic peak current versus square root of scan rate plot; **c** electrochemical impedance spectra of 33G low content co-axial PAN/Si 50 nm fibrous asymmetric membrane electrode. Inset in **c** is the equivalent circuit used for fitting

SEI layer throughout the 300 cycles. In contrast, the charge transfer resistance of the membrane electrode at the 1st cycle is about twice as much as that of other cycles because a stable SEI layer has not been fully developed yet and the

native non-conductive layer on Si particle consisting of silicon oxide and silanol has not been efficiently broken down to lower charge transfer resistance [54]. The Nyquist plots were fitted using an equivalent circuit shown in Fig. 7c, where R_s is the total resistance of electrolyte, separator, and electrodes at the high frequency, R_{ct} and R_{SEI} represent the charge transfer, and interfacial SEI resistances at lower frequencies, CPE stands for the constant phase element related to the double layer capacitance and W_d is the finite-length Warburg diffusion impedance [55]. The fitted data (S9) show that R_{ct} stays around 200 ohms without much change during the cycling test. However, there is a significant reduction in R_{SEI} between the 1st and 100th cycles (138 to 59 ohms). R_{SEI} values at 100th, 200th, and 300th cycles are very close to each, further confirming the formation of stable interfacial layer and being consistent with the cycling performance and SEM examinations (S8).

We also opened the cycled cell containing co-axial silicon fibrous asymmetric membrane for SEM imaging and elemental mapping (S8). No cracks were observed on the top surface of the fiber, indicating the formation of integral and stable SEI layer as the result of its unique co-axial asymmetric porous structure that can efficiently withstand the large volume expansion of Si-based anodes.

4 Conclusions

Eight types of fibrous Si asymmetric membranes have been prepared to explore the effects of Si particle size, Si concentration, type of polymer, fiber diameter, and co-axial coating on their electrochemical performance as lithium-ion battery anode. In general, smaller Si particle, lower Si concentration, smaller fiber diameter, and co-axial coating can significantly enhance both capacity and cyclability. Membranes made using PAN demonstrate better electrochemical performance because carbonized PAN is not only mechanically strong but also electrically conductive. Co-axial fibrous Si asymmetric membrane possesses the most outstanding cycling performance because of its unique 3-D, co-axial, porous structure that can efficiently accommodate large volume expansion, prohibit the loss of fractured Si particles, and facilitate the formation of stable SEI layer. The asymmetric membrane electrode can be fabricated continuously at a high speed using an adapted method from water purification industry (hollow fiber membranes), thereby significantly reducing the fabrication cost and increasing the commercialization potential of Si-based anodes.

Acknowledgements This work is supported by National Science Foundation Division of Chemical, Bioengineering, Environmental and Transport Systems (NSF CBET Award #1800619). JW, CA, PB, and

SX sincerely acknowledge the generous support provided by Georgia Southern University. C.J. and A.S. thank the support from State University of New York at Binghamton.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Chen H, Cong TN, Yang W, Tan C, Li Y, Ding Y (2009) Progress in electrical energy storage system: a critical review. *Prog Nat Sci* 19(3):291–312. <https://doi.org/10.1016/j.pnsc.2008.07.014>
- Tarascon J-M (2010) Key challenges in future Li-battery research. *Philos Trans R Soc A* 368(1923):3227–3241. <https://doi.org/10.1098/rsta.2010.0112>
- Armand M, Tarascon JM (2008) Building better batteries. *Nature* 451:652. <https://doi.org/10.1038/451652a>
- Nitta N, Wu F, Lee JT, Yushin G (2015) Li-ion battery materials: present and future. *Mater Today* 18(5):252–264. <https://doi.org/10.1016/j.mattod.2014.10.040>
- Kim H, Lee E-J, Sun Y-K (2014) Recent advances in the Si-based nanocomposite materials as high capacity anode materials for lithium ion batteries. *Mater Today* 17(6):285–297. <https://doi.org/10.1016/j.mattod.2014.05.003>
- Su X, Wu Q, Li J, Xiao X, Lott A, Lu W, Sheldon BW, Wu J (2014) Silicon-based nanomaterials for lithium-ion batteries: a review. *Adv Energy Mater* 4(1):1300882. <https://doi.org/10.1002/aenm.201300882>
- Feng K, Li M, Liu W, Kashkooli AG, Xiao X, Cai M, Chen Z (2018) Silicon-based anodes for lithium-ion batteries: from fundamentals to practical applications. *Small* 14(8):1702737. <https://doi.org/10.1002/smll.201702737>
- Wu H, Chan G, Choi JW, Ryu I, Yao Y, McDowell MT, Lee SW, Jackson A, Yang Y, Hu L, Cui Y (2012) Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nat Nanotechnol* 7:310. <https://doi.org/10.1038/nnano.2012.35>
- Wang C, Wu H, Chen Z, McDowell MT, Cui Y, Bao Z (2013) Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. *Nat Chem* 5:1042. <https://doi.org/10.1038/nchem.1802>
- Magasinski A, Zdyrko B, Kovalenko I, Hertzberg B, Burtovyy R, Huebner CF, Fuller TF, Luzinov I, Yushin G (2010) Toward efficient binders for Li-ion battery Si-based anodes: polyacrylic acid. *ACS Appl Mater Interfaces* 2(11):3004–3010. <https://doi.org/10.1021/am100871y>
- Kumar SK, Ghosh S, Malladi SK, Nanda J, Martha SK (2018) Nanostructured silicon-carbon 3D electrode architectures for high-performance lithium-ion batteries. *ACS Omega* 3(8):9598–9606. <https://doi.org/10.1021/acsomega.8b00924>
- Benítez A, Lecce D, Elia GA, Caballero Á, Morales J, Hassoun J (2018) A lithium-ion battery using a 3 D-array nanostructured graphene-sulfur cathode and a silicon oxide-based anode. *ChemSuschem* 11(9):1512–1520. <https://doi.org/10.1002/cssc.201800242>
- Liu J, Kopold P, van Aken PA, Maier J, Yu Y (2015) Energy storage materials from nature through nanotechnology: a sustainable route from reed plants to a silicon anode for lithium-ion batteries. *Angew Chem Int Ed* 54(33):9632–9636. <https://doi.org/10.1002/anie.201503150>
- Zhao C, Wada T, De Andrade V, Gürsoy D, Kato H, Y-cK Chen-Wiegart (2018) Imaging of 3D morphological evolution of nanoporous silicon anode in lithium ion battery by X-ray nano-tomography. *Nano Energy* 52:381–390. <https://doi.org/10.1016/j.nanoen.2018.08.009>
- Magasinski A, Dixon P, Hertzberg B, Kvit A, Ayala J, Yushin G (2010) High-performance lithium-ion anodes using a hierarchical bottom-up approach. *Nat Mater* 9:353. <https://doi.org/10.1038/nmat2725>
- Xia F, Kim SB, Cheng H, Lee JM, Song T, Huang Y, Rogers JA, Paik U, Park WI (2013) Facile synthesis of free-standing silicon membranes with three-dimensional nanoarchitecture for anodes of lithium ion batteries. *Nano Lett* 13(7):3340–3346. <https://doi.org/10.1021/nl401629q>
- Jin Y, Zhu B, Lu Z, Liu N, Zhu J (2017) Challenges and recent progress in the development of si anodes for lithium-ion battery. *Adv Energy Mater* 7(23):1700715. <https://doi.org/10.1002/aenm.201700715>
- Petersen RJ (1993) Composite reverse osmosis and nanofiltration membranes. *J Membr Sci* 83(1):81–150. [https://doi.org/10.1016/0376-7388\(93\)80014-O](https://doi.org/10.1016/0376-7388(93)80014-O)
- Radjenović J, Petrović M, Ventura F, Barceló D (2008) Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. *Water Res* 42(14):3601–3610. <https://doi.org/10.1016/j.watres.2008.05.020>
- Nicolaisen B (2003) Developments in membrane technology for water treatment. *Desalination* 153(1):355–360. [https://doi.org/10.1016/S0011-9164\(02\)01127-X](https://doi.org/10.1016/S0011-9164(02)01127-X)
- Cadotte JE, Petersen RJ, Larson RE, Erickson EE (1980) A new thin-film composite seawater reverse osmosis membrane. *Desalination* 32:25–31. [https://doi.org/10.1016/S0011-9164\(00\)86003-8](https://doi.org/10.1016/S0011-9164(00)86003-8)
- Wu J, Chen H, Padgett C (2016) Silicon asymmetric membranes for efficient lithium storage: a scalable method. *Energy Technol* 4(4):502–509. <https://doi.org/10.1002/ente.201500315>
- Wu J, Chen H, Byrd I, Lovelace S, Jin C (2016) Fabrication of SnO₂ asymmetric membranes for high performance lithium battery anode. *ACS Appl Mater Interfaces* 8(22):13946–13956. <https://doi.org/10.1021/acsami.6b03310>
- Wu J, Byrd I, Jin C, Li J, Chen H, Camp T, Bujol R, Sharma A, Zhang H (2017) Reinvigorating reverse-osmosis membrane technology to stabilize the V₂O₅ lithium-ion battery cathode. *ChemElectroChem* 4(5):1181–1189. <https://doi.org/10.1002/celec.201701012>
- Byrd I, Chen H, Webber T, Li J, Wu J (2015) Self-assembled asymmetric membrane containing micron-size germanium for high capacity lithium ion batteries. *RSC Adv* 5(113):92878–92884. <https://doi.org/10.1039/C5RA19208K>
- van de Witte P, Dijkstra PJ, van den Berg JWA, Feijen J (1996) Phase separation processes in polymer solutions in relation to membrane formation. *J Membr Sci* 117(1):1–31. [https://doi.org/10.1016/0376-7388\(96\)00088-9](https://doi.org/10.1016/0376-7388(96)00088-9)
- Wang R, Shi L, Tang CY, Chou S, Qiu C, Fane AG (2010) Characterization of novel forward osmosis hollow fiber membranes. *J Membr Sci* 355(1):158–167. <https://doi.org/10.1016/j.memsci.2010.03.017>
- Bottino A, Capannelli G, Munari S (1986) Factors affecting the structure and properties of asymmetric polymeric membranes. In: Drioli E, Nakagaki M (eds) *Membranes and membrane processes*. Springer, Boston, pp 163–178. https://doi.org/10.1007/978-1-4899-2019-5_17
- Cocciantelli JM, Ménétrier M, Delmas C, Doumerc JP, Pouchard M, Broussely M, Labat J (1995) On the $\delta \rightarrow \gamma$ irreversible transformation in Li/V₂O₅ secondary batteries. *Solid State Ionics* 78(1–2):143–150. [https://doi.org/10.1016/0167-2738\(95\)00015-X](https://doi.org/10.1016/0167-2738(95)00015-X)
- Du Z, Wood DL, Daniel C, Kalnaus S, Li J (2017) Understanding limiting factors in thick electrode performance as applied to high

- energy density Li-ion batteries. *J Appl Electrochem* 47(3):405–415. <https://doi.org/10.1007/s10800-017-1047-4>
31. Pinnau I, Koros WJ (1991) Structures and gas separation properties of asymmetric polysulfone membranes made by dry, wet, and dry/wet phase inversion. *J Appl Polym Sci* 43(8):1491–1502. <https://doi.org/10.1002/app.1991.070430811>
 32. Kim I-C, Yun H-G, Lee K-H (2002) Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process. *J Membr Sci* 199(1):75–84. [https://doi.org/10.1016/S0376-7388\(01\)00680-9](https://doi.org/10.1016/S0376-7388(01)00680-9)
 33. Lee K-W, Seo B-K, Nam S-T, Han M-J (2003) Trade-off between thermodynamic enhancement and kinetic hindrance during phase inversion in the preparation of polysulfone membranes. *Desalination* 159(3):289–296. [https://doi.org/10.1016/S0011-9164\(03\)90081-6](https://doi.org/10.1016/S0011-9164(03)90081-6)
 34. Barth C, Gonçalves MC, Pires ATN, Roeder J, Wolf BA (2000) Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance. *J Membr Sci* 169(2):287–299. [https://doi.org/10.1016/S0376-7388\(99\)00344-0](https://doi.org/10.1016/S0376-7388(99)00344-0)
 35. Ferrari AC (2007) Raman spectroscopy of graphene and graphite: disorder, electron–phonon coupling, doping and nonadiabatic effects. *Solid State Commun* 143(1):47–57. <https://doi.org/10.1016/j.ssc.2007.03.052>
 36. Meier C, Lüttjohann S, Kravets VG, Nienhaus H, Lorke A, Wiggers H (2006) Raman properties of silicon nanoparticles. *Phys E* 32(1):155–158. <https://doi.org/10.1016/j.physe.2005.12.030>
 37. Misra S, Liu N, Nelson J, Hong SS, Cui Y, Toney MF (2012) In situ X-ray diffraction studies of (de)lithiation mechanism in silicon nanowire anodes. *ACS Nano* 6(6):5465–5473. <https://doi.org/10.1021/nn301339g>
 38. Mondal T, Bhowmick AK, Krishnamoorti R (2012) Chlorophenyl pendant decorated graphene sheet as a potential antimicrobial agent: synthesis and characterization. *J Mater Chem* 22(42):22481–22487. <https://doi.org/10.1039/C2JM33398H>
 39. Wang S, Chen Z-H, Ma W-J, Ma Q-S (2006) Influence of heat treatment on physical–chemical properties of PAN-based carbon fiber. *Ceram Int* 32(3):291–295. <https://doi.org/10.1016/j.ceramint.2005.02.014>
 40. Huang X (2009) Fabrication and properties of carbon fibers. *Materials* 2(4):2369
 41. Reynolds WN, Moreton R, Worthington PJ (1980) Some factors affecting the strengths of carbon fibres [and discussion]. *Philos Trans R Soc Lond Ser A* 294(1411):451–461
 42. He JW, Xu X, Corneille JS, Goodman DW (1992) X-ray photoelectron spectroscopic characterization of ultra-thin silicon oxide films on a Mo(100) surface. *Surf Sci* 279(1):119–126. [https://doi.org/10.1016/0039-6028\(92\)90748-U](https://doi.org/10.1016/0039-6028(92)90748-U)
 43. An SJ, Li J, Daniel C, Mohanty D, Nagpure S, Wood DL (2016) The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon* 105:52–76. <https://doi.org/10.1016/j.carbon.2016.04.008>
 44. Fitzer E (1989) Pan-based carbon fibers—present state and trend of the technology from the viewpoint of possibilities and limits to influence and to control the fiber properties by the process parameters. *Carbon* 27(5):621–645. [https://doi.org/10.1016/0008-6223\(89\)90197-8](https://doi.org/10.1016/0008-6223(89)90197-8)
 45. Ding N, Xu J, Yao YX, Wegner G, Fang X, Chen CH, Lieberwirth I (2009) Determination of the diffusion coefficient of lithium ions in nano-Si. *Solid State Ionics* 180(2):222–225. <https://doi.org/10.1016/j.ssi.2008.12.015>
 46. Liu XH, Zhong L, Huang S, Mao SX, Zhu T, Huang JY (2012) Size-dependent fracture of silicon nanoparticles during lithiation. *ACS Nano* 6(2):1522–1531. <https://doi.org/10.1021/nn204476h>
 47. Singh M, Kaiser J, Hahn H (2015) Thick electrodes for high energy lithium ion batteries. *J Electrochem Soc* 162(7):A1196–A1201. <https://doi.org/10.1149/2.0401507jes>
 48. Wood M, Li J, Wood DL, Daniel C, Dunlop AR, Polzin BJ, Jansen AN, Krumdieck G (2018) Evaluation of thick electrode architectures for high energy density Li-ion batteries. *Meeting Abstracts MA2018-01(3):253*
 49. Chen LB, Xie JY, Yu HC, Wang TH (2009) An amorphous Si thin film anode with high capacity and long cycling life for lithium ion batteries. *J Appl Electrochem* 39(8):1157–1162. <https://doi.org/10.1007/s10800-008-9774-1>
 50. Obrovac MN, Krause LJ (2007) Reversible cycling of crystalline silicon powder. *J Electrochem Soc* 154(2):A103–A108. <https://doi.org/10.1149/1.2402112>
 51. Pereira-Nabais C, Światowska J, Chagnes A, Ozanam F, Gohier A, Tran-Van P, Cojocaru C-S, Cassir M, Marcus P (2013) Interphase chemistry of Si electrodes used as anodes in Li-ion batteries. *Appl Surf Sci* 266:5–16. <https://doi.org/10.1016/j.apsusc.2012.10.165>
 52. McCormac K, Byrd I, Brannen R, Seymour B, Li J, Wu J (2015) Preparation of porous Si and TiO₂ nanofibres using a sulphur-templating method for lithium storage. *Physica Status Solidi* 212(4):877–881. <https://doi.org/10.1002/pssa.201431834>
 53. Wang Z, Su Q, Deng H, He W, Lin J, Fu YQ (2014) Modelling and simulation of electron-rich effect on Li diffusion in group IVA elements (Si, Ge and Sn) for Li ion batteries. *J Mater Chem A* 2(34):13976–13982. <https://doi.org/10.1039/C4TA01614A>
 54. Wu JJ, Bennett WR (2012) Fundamental investigation of Si anode in Li-Ion cells. In: 2012 IEEE Energytech, 29–31. pp 1–5. <https://doi.org/10.1109/energytech.2012.6304667>
 55. Väli R, Jänes A, Lust E (2017) Alkali-metal insertion processes on nanospheric hard carbon electrodes: an electrochemical impedance spectroscopy study. *J Electrochem Soc* 164(11):E3429–E3437. <https://doi.org/10.1149/2.0431711jes>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Affiliations

Ji Wu¹ · Christopher Anderson¹ · Parker Beaupre¹ · Shaowen Xu² · Congrui Jin³ · Anju Sharma⁴

¹ Department of Chemistry and Biochemistry, Georgia Southern University, 250 Forest Drive, Statesboro, GA 30460, USA

² Department of Mechanical Engineering, Georgia Southern University, 1100 Statesboro Pl Cir, Statesboro, GA 30460, USA

³ Department of Mechanical Engineering, Binghamton University, 4400 Vestal Parkway East, Binghamton, NY 13902, USA

⁴ Small Scale Systems Integration and Packaging (S3IP) Center, Binghamton University, Binghamton, NY 13902, USA