Amorphous silicon nanowires (a-SiNWs) have been prepared by electrospinning a liquid silane-based precursor. Cyclohexasilane (Si₆H₁₂) was admixed with poly(methyl methacrylate) (PMMA) in toluene giving an ink that was electrospun into the a-SiHₓ/PMMA wires with diameters of 50–2000 nm. Raman spectroscopy revealed that thermal treatment at 350°C transforms this deposit into a-SiNWs. These materials were coated with a thin carbon layer and then tested as half-cells where a reasonable plateau in electrochemical cycling was observed after an initial capacity fade. Additionally, porous a-SiNWs were realized when the thermally decomposable binder polypropylene carbonate/poly(cyclohexene carbonate) was used as the polymer carrier.

Figure 1. Schematic illustrating the transformation of Si₆H₁₂ into electronic materials.

Hg/cm²
square sheet of aluminum foil (2 mil Reynolds Wrap) was placed on a grounding pad with a standoff distance of ~12 in. from the needle. A high voltage source (Gamma High Voltage Research, model ES40P-12W/DDPM) was connected with the positive terminal on the needle and the negative (ground) on the aluminum foil. The syringe pump was set to a flow rate of 0.4 mL/h and allowed to run until the needle was primed with liquid. Once a droplet formed on the outside of the needle, the power source was adjusted to 15 kV.

The electrospun deposits were transformed into amorphous silicon via thermal treatment by placing the foil substrate onto a room temperature hotplate (also located inside the N₂-filled glove box), which was ramped to ~350°C and held for 20 min. The morphological development was assayed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a JEOL JSM-6490LV and a JEOL JEM-2100 LaB₆, respectively. Phase identification was carried out via analysis of the transverse orthogonal (TO) mode using a Horiba Jobin Yvon (LabRAM ARAMIS) confocal Raman microscope. Two polymers were used as the carriers for electrospinning and each was processed in a slightly different manner (see below).

The electrospun nanowire materials were used in making anodes in electrochemical cells. Before assembly in pouch cells, the a-SiNWs were exposed to air and loaded into a CVD chamber where a thin conducting carbon layer (~10 nm thick) was deposited. Afterwards, the C-coated a-SiNWs were moved into a second inert atmosphere argon-filled glove box (H₂O and O₂ < 1 ppm). Lithium metal/a-SiNW half-cells were fabricated using Celgard 2300 as the separator and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1) as the electrolyte with a mass loading of ~4 mg/cm². Electrochemical testing was performed by cycling between 0.02 and 1.50 V at 100 mA/g using an Arbin model B2000 tester.

Results and Discussion

The first ink was composed of a nominally 70:30 wt % ratio of PMMA/Si₆H₁₂ in toluene. After electrospinning, the continuous PMMA/Si₆H₁₂ was transformed thermally to give wire diameters that ranged from micrometer-sized to ~150 nm, as observed by SEM, with some wires interspersed with beads/globules (see Fig. S1 of supplementary materials). The TEM analyses showed a second type of wires with little variability in the radial dimension and diameters in the 15–30 nm range (Fig. 2a). The marked variation in the radial dimension (i.e., beads/globules) is ascribed to the unrefined microfluidics of this polymer mixture. The 350°C treatment causes Si₆H₁₂ to transform first to polysilane and then into a-Si, as evidenced by Raman spectroscopy. No crystalline phase was observed in the Raman spectra where the Si–Si TO bonding mode shifts from a broad peak around 460 cm⁻¹ for polysilane to a less broad peak at 480 cm⁻¹ for amorphous silicon to a sharp peak at 520 cm⁻¹ for polycrystalline silicon.¹⁸

Figure 3 shows the charge/discharge data for the a-Si nanowires prepared from the PMMA/Si₆H₁₂ ink. The first silicon specific discharge capacity is 840 mAh/g with 410 mAh/g observed after 30 cycles. The discharge capacity in this graph is relatively low as compared to the literature where carbon-coated silicon typically gives ≥1000 mAh/g.¹⁸,²⁰ There are several factors that might explain the lower-than-desired materials metrics presented in this initial article. First, the percentage of Si in the final anode is likely less than the 28% Si mass fraction in the electrospinning ink but we are unable to perform an accurate correction given the CVD process variations (i.e., C:Si is typically ~0.04 to 0.08). Second, the wires were exposed to air before assembly of the battery, which could have caused oxidation and a concomitant reduction in the amount of silicon available to intercalate lithium. Third, residual PMMA within the electrospun wires may have inhibited lithiation. A favorable outcome of this preliminary article is the resilience of the cell to cycling where capacity decreased only 9.2% from the second to the 30th cycle. The trend in this data compares well with a previous article by Wang and Kumta and would support a premise that these a-Si nanowires retain mechanical stability during the cycling tests.

Figure 2. TEM micrographs of electrospun nanowires formed (a) from a PMMA/Si₆H₁₂-based ink where diameters from 33 to 16 nm are noted and (b) from a QPAC100/Si₆H₁₂-based ink showing the porous nature observed after thermolysis of the polymer.

Figure 3. Charge/discharge data for a half-cell comprised of lithium metal foil and C-coated a-Si wires.
Barring any undesirable chemical reactivity with Si–Si or Si–H bonds, particles of carbon, metals, and solid electrolytes may be introduced into liquid silane-based electrospinning inks using standard dispersion chemistry. Because the spun wires convert to amorphous silicon at relatively low temperature, formation of excessive surface oxide and carbide phases can be avoided, which otherwise negatively affect capacity and rate capabilities. Finally, other routes to SiNWs yield crystalline products that become amorphous after lithium intercalation in LIBs.

Perhaps surprisingly, we have observed that the liquid silane monomer is relatively unaffected by the high voltage electrospinning process and remains associated with the polymeric carrier (i.e., PMMA or QPAC 100) upon evaporation of the toluene solvent. Light- or heat-induced radical polymerization of the Si₆H₁₂ gives a viscous polydihydrosilane deposit that assumes a geometry that is related to the structure of the copolymer. The structure of the silicon nanowires prepared from Si₆H₁₂/polymer in toluene inks appears to be governed by the physics of the mixtures. For example, the SEM data shows a fibrous structure after annealing an electrosprun composite formed from a 1.0:2.6 wt % ratio of Si₆H₁₂:PPMA in toluene ink. We speculate that this structure is related to the wetting of the polymer by the liquid silane (Fig. 2a). By way of comparison, the treatment of the composite formed by electrospinning a 1.0:2.0 wt % ratio of Si₆H₁₂:QPAC 100 in toluene precursor gives a porous wire (Fig. 2b) that may be a consequence of the immiscibility of Si₆H₁₂ and the polymer carrier after solvent evaporation.

There are other articles of electrospinning silicon-containing nanostructures. The approach reported herein has advantages compared to electrospun inks that contain dispersed Si particles in poly(acrylonitrile)21,22 as the latter requires appropriate surface functionalization of the silicon particles to promote dispersion while avoiding flocculation. In addition, others have reported silicon nanowires via electrospinning where the electrospun polymer fiber serves as a template for the growth of the silicon coatings by the hot-wire CVD23 or the plasma-enhanced chemical vapor deposition (PECVD).24 While these routes allow the growth of a-Si nanowires with hollow cores, hot-wire and PECVD are prone to poor precursor utilization and traditionally slow growth rates.

The ability to electrosprin SiNWs offers additional benefits in terms of transformational advancements in energy-related materials and devices. Toward that end, silicon nanowire-based solar cells25,26 and thermoelectrics27 have been reported. While extraordinary possibilities might be envisioned, these potential applications shall remain an academic curiosity until the large-scale production of SiNWs becomes a reality. Future work may include evaluation of needless electrospinning methodologies as a way of realizing higher throughput. Additionally, the ability to scale up the production of the Si₆H₁₂ starting material is a primary focus of our research team at present. Possibly, with the appropriate process control and precursor formulation, the electrospinning a-SiNW technology that is being tested for anodes in LIBs may also be enabling for Si nanowire-based solar cells and thermoelectrics.

Conclusions

We have reported the first route to a-SiNWs and utilized an electrospinning method that employs a liquid silane/polymer in toluene precursor. The morphology of the electrosprun materials can be modified through the use of a pore-forming polymer carrier, and thereby, we report the first porous a-SiNWs as well. The electrosprun a-SiNWs exhibit a good electrochemical response with little fade after the second cycle (i.e., after the formation of a solid electrolyte interphase layer).28 While some hurdles remain before large-scale production of a-SiNW lithium ion battery anodes (e.g., scale-up of Si₆H₁₂ and multijet electrospinning), we have demonstrated the materials science of this process, and deployment of this technology appears to depend mainly on engineering process optimization and cost reduction of the Si₆H₁₂ starting material.

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17. See supplementary material at http://dx.doi.org/10.1149/1.3466994 (E-ESLEF6-13-013010) for additional information.