Supporting information

Recycling Silicon Photovoltaic Cells into Silicon Anodes for Li-ion Batteries Using 3D Printing

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1 Experimental Section

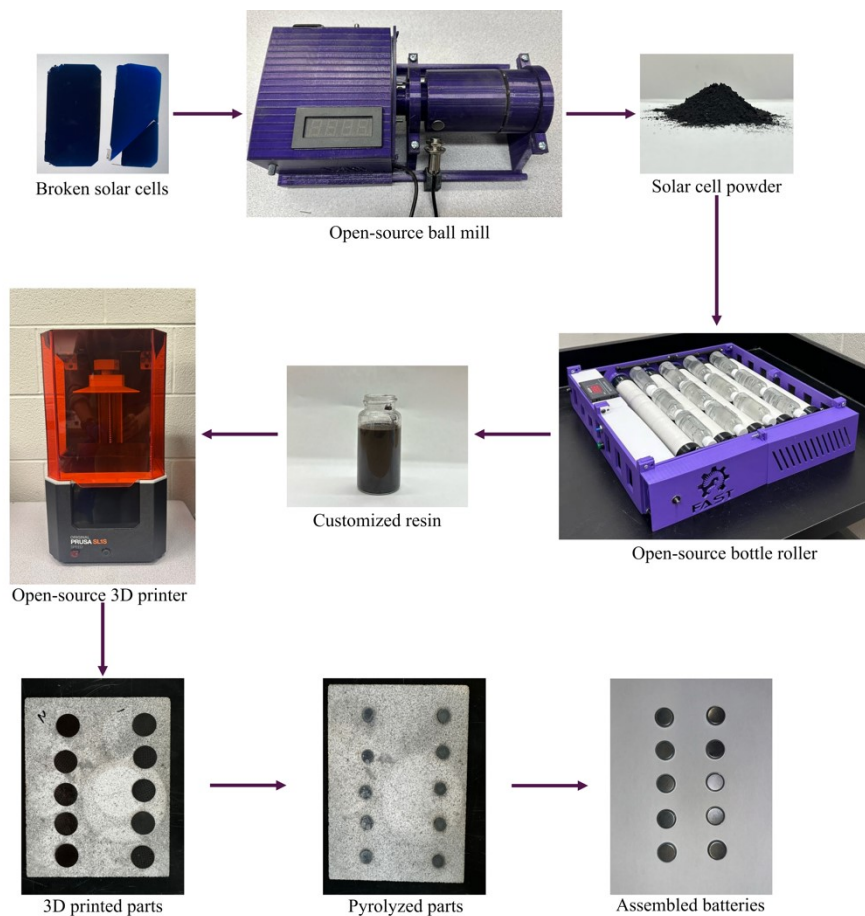The schematic of the processing steps is shown in Figure S1.

Figure S1. Processing steps for recycling silicon solar cells into batteries.

1.1 Materials

The broken c-Si-based solar photovoltaic cells were acquired from Heliene Inc. (Sault Ste. Marie, Ontario, Canada). The dispersant used here is cetyltrimethylammonium bromide (CTAB) (Sigma Aldrich, Ontario, Canada). The Prusament resins (transparent red, transparent amber, transparent blue, orange, and flexible) are purchased from the official Prusa Research (Prague, Czech Republic), the Anycubic resins (black and grey) are ordered from amazon.ca, and the 3DRS resins (colorbase, hard grey, white) are obtained from 3D Printing Canada (Ontario, Canada). Bis(2,4,6-Trimethylbenzoyl) phenylphosphine oxide is used as the photoinitiator which is provided from IGM resins (Charlotte, North Carolina). The 32μm mesh size sieve from KimLab (Ontario, Canada).

1.2 Resin fabrication

The processing steps are illustrated in Figure S1. The broken solar cells were ground down using the open-source ball mill [1]. The ground solar waste was sieved with 32 micrometer sieves. To remove impurities from the broken solar cell powder, a washing process was carried out, as explained in the literature. Specifically, 9.0 g of broken solar cell powder was mixed with 150 mL of

37 wt% HCl. The mixture was stirred and heated to 80°C for 1 hour. After 1 hour, the mixture was allowed to cool to room temperature, and the solid residue was then filtered to obtain the purified silicon material and was placed in the oven in 60⁰C overnight[2]. Then the powder was mixed with 2% of the solid load CTAB as the dispersant and 1% of the resin photoinitiator. After that, the polymer resin was added to the powder. The solid load was 12wt% of the resin. The solution was moved into dark bottles to prevent the resin from curing. Using the open-source bottle roller[3], the mixture was mixed overnight to make a homogenous customized resin to be used in SLA printer.

1.3 3D printing of customized resin
For this step, the coin-shape anodes were designed with Onshape[4], and sliced in the PrusaSlicer[5]. The design and all data for this article are available on the Open Science Framework [6]. A series of experiments was carried out to determine the most suitable combination of layer thickness and exposure time to print the sample. Because the silicon resin requires a longer curing period than standard polymer resin without additives, its complete polymerization is the primary consideration in selecting the printing parameters. Different curing times were evaluated through trial and error to identify the shortest time that would cause each resin to adhere properly while minimizing the print time. For the initial layer, curing times under 35 seconds resulted in film breakage and incomplete bonding of the polymer resin to the build plate, which caused print failures. As a result, 35 seconds was used as the minimum time needed to adhere the polymer resin to the build plate. Similarly, the silicon resin required at least 40 seconds to fully polymerize as curing it for any shorter duration led to insufficient curing and failed prints. Layer thickness values of 0.01 mm, 0.03 mm, and 0.05 mm were also evaluated. A 0.01 mm layer thickness was not suitable due to insufficient curing and long printing times, whereas a 0.05 mm thickness prevented proper light penetration through the resin and led to print failures. Among these options, a 0.03 mm layer thickness was optimal, which resulted in successful print while maintained sufficient resolution and acceptable print speed. After that, the samples were printed using Original Prusa SL1S SPEED 3D printer (Prague, Czech Republic). In this step multi-material printing was done. For this purpose, one vat was poured with the flexible resin, and the other one was poured with the customized resin. Since the customized resin caused contamination in the vat which affects the print quality in the future, an open-source vat [7] was used for this purpose. The vat containing the flexible resin was placed in the printer and the print was started. In this step, when the machine started to print the first layer, pause/ stop was clicked. After the printer finishes printing the first layer, the build platform goes up and the vat is replaced by that for the customized resin. Then, the print is resumed. After the print finishes, the printed parts were separated from the build platform by a scraper. In this step, the layer printed by the flexible resin can be separated easily. Then, the printed part was put in a curing machine that the excess resin that was uncured gets cured.

1.4 Pyrolysis
The printed samples were placed in a gas-sealed box furnace, Model 1616 FL (CM Furnaces, USA), for pyrolysis. The samples were heated up to 850°C with 1°C/ min and the temperature was increased to 1400°C with 3°C/ min and they were kept in this temperature for 2h. After that, the furnace was cooled down to the room temperature with 10°C/ min rate.

1.5 Material tests
The Ocean Insight FLAME spectrometer was used to measure the absorbance index of different resin types before and after adding the solid load [8]. The samples were scanned over the selected wavelength range of 200-800 nm and the absorbance was recorded. To analysis the amount of carbon in different types of the resins, DTA and TGA tests were conducted using Netzsch STA 409 (Netzsch Gmbh, Selb, Germany) at 10 °C min^{-1} up to 1200 °C in flowing Air/N2 (150 cc min^{-1}), to measure the carbon content after pyrolysis in an air atmosphere with a flow rate of 30 ml/min, starting from room temperature and heating to 800⁰C at a rate of 10⁰C min^{-1}. OpenFlexure Microscope from IO Rodeo was used to measure the dimensions of the printed parts [9] . A scanning electron microscope (SEM) image was conducted to see the morphology and microstructure. Energy dispersive X-Ray (EDX) was used to identify the type of elements that are present as well as the percentage of each element concentration within the pyrolyzed samples. SEM and EDX were conducted using Hitachi SU3500 scanning electron microscope with an Oxford Instruments X-act EDX detector (Hitachi, Japan, Oxford instruments UK). X-Ray diffraction (XRD) was performed using Bruker D8 advance x ray diffractometer (Bruker Gmbh, Germany), to analyze the phase and crystallinity of the samples after the pyrolysis. Raman spectroscopy was performed using a Raman microscope with a 514 nm laser excitation source (Renishaw, UK), to characterize the chemical structure of the pure transparent red resin samples before and after pyrolysis.

1.6 Electrochemical tests

The electrochemical performance of the fabricated anodes was evaluated using CR2032 coin cells. The assembly of these cells was conducted in an argon-filled glove box with oxygen and moisture levels maintained below 0.1 ppm. Celgard 2400 was used as the separator, and the electrolyte was composed of 1 M LiPF6 in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) in a 1:1:1 volume ratio with a fluoroethylene carbonate (FEC) additive. The chemicals were provided from Gotion, USA. Lithium metal (China) served as both the counter and reference electrode. Electrochemical tests were performed using CS300 model potentiostatt from Corrtest, China. Cyclic voltammetry was performed using the potential in the range of 0.01 to 2.5 V (vs. Li+/Li) with a scan rate of 0.1 mV/s. Galvanostatic charge-discharge testing was carried out in the voltage range of 0.01 to 1.5 V (vs. Li/Li+) at a current rate of 1C. The mass of solid load was calculated as 0.0015 gr in the anode.
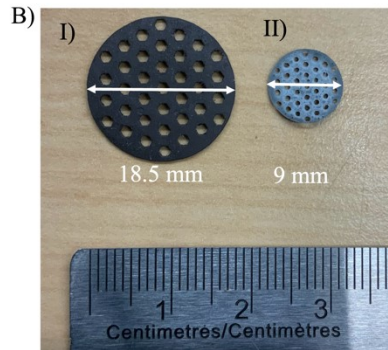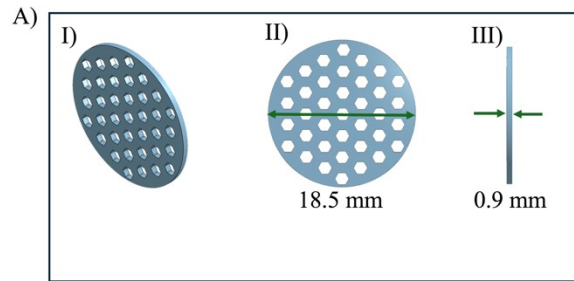
Figure S2. A) CAD model of the designed anode (I) Isometric view, (II) front view (diameter), and (III) side view (thickness), B) pictures of the (I) as-printed sample, and (II) pyrolyzed sample, C) the measured thickness of the as-printed sample, and D) the measured thickness of the pyrolyzed sample.
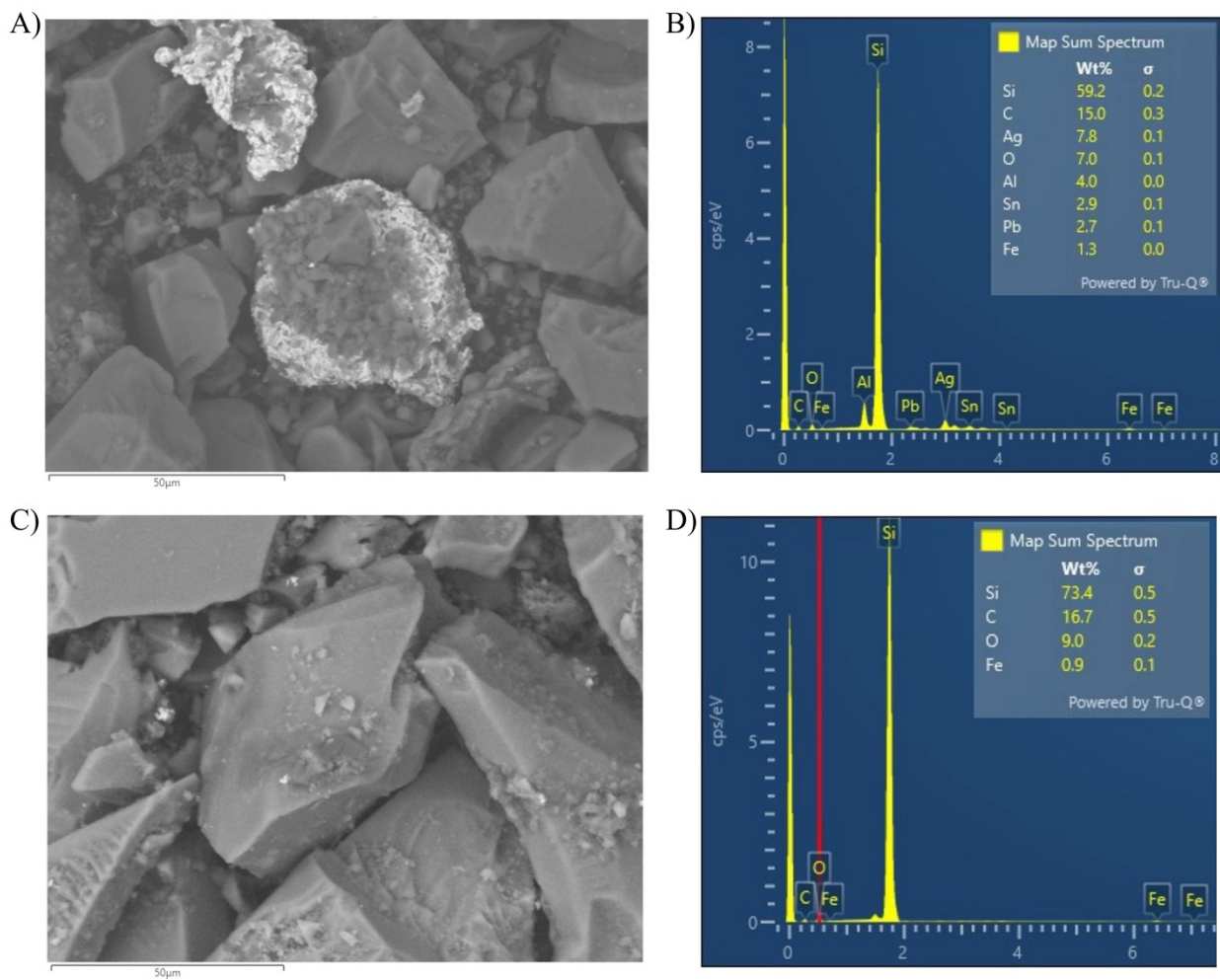
Figure S3. SEM image of A and B) as ball milled solar cell powder, C and D) acid washed solar cell powder after ball milling

2 References

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