Supporting Information

Primary Corrosion Processes for Polymer Embedded Free-Standing or Substrate-Supported Silicon Microwire Arrays in Aqueous Alkaline Electrolytes

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Sample cleaning procedure

Chips of approximately 5 cm x 2 cm were scribed from this wafer of wire arrays. The wire arrays were cleaned using a standard Radio Corporation of America (RCA) procedure, in which the samples were first cleaned in a Standard Clean 1 bath, 5:1:1 $H_2O/NH_4OH/H_2O_2$ at 80 °C for >10 min. The samples were then dipped into Buffered oxide etchant (6:1 (v/v) 40% NH_4F to 49% HF; Transene Inc.) for 5 min at 20 °C, and were then removed and immediately rinsed with >18 Mohm-cm resistivity deionized water and blown dry under a stream of $N_2(g)$. A RCA Standard Clean 2 bath, 6:1:1 $H_2O/HCl/H_2O_2$ at 70 °C for >10 min was used to remove SiO_2, Al_2O_3 and trace metal impurities. Hydrogen Peroxide 30% (w/w) Solution GR ACS was obtained from Millipore Sigma, and Ammonia solution 28.0 - 30.0% (w/w) was obtained from

J.T. Baker. Hydrochloric Acid GR ACS 36.5-38.0% (w/w) was obtained from Millipore Sigma. All chemicals were used as received.

Sample assembly

The on-substrate samples were placed in a Falcon polystyrene petri dish, and Loctite EA9460 epoxy was used to seal all exposed edges and secure the sample to the bottom of the petri dish. The bottom of another four Falcon polystyrene petri dishes was covered with a 10:10:1 mixture by weight of polydimethylsiloxane (PDMS) from Sylguard® elastomer silicone base, toluene (Millipore Sigma ≥ 99.5%, GR ACS), and Sylguard® 184 silicone elastomer curing agent, and cured on glass slides using a VWR hot plate at 75°C for 24 h. The four free-standing samples were placed in these petri dishes, and again were placed on glass slides on a VWR hot plate at 75 °C for 1 h to bind the PDMS layers.

Fifty milliliters of 1.0 M KOH(aq) (Sigma-Aldrich ≥85% KOH basis, pellets) was prepared and poured into each of the 8 petri dishes, such that each sample was well covered by the liquid. All samples were then left in the dark, with pairs of one on-substrate sample and one free-standing sample removed after 24 h, 48 h, 168 h, and 240 h of immersion time.

Removal of sample from KOH

As each sample was removed, the KOH(aq) was poured out and the sample was rinsed thoroughly with 18.3 MΩ-cm deionized H_2O. The samples were then blown dry under a stream of N_2(g) and placed in a Napco 5831 Vacuum Oven for 1 h at room temperature.

Statistics for Optically Identified Etched Wires

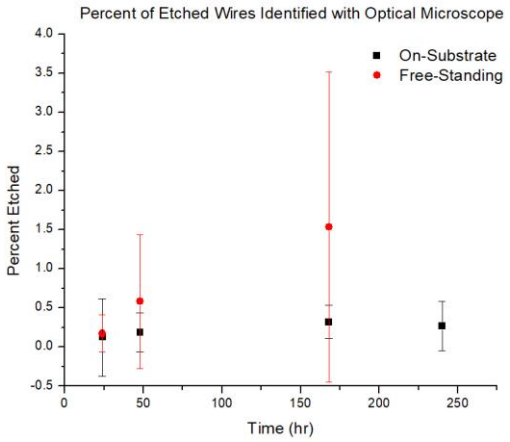

Figure S1. Percent of etched wires seen with the optical microscope, with averages given across multiple fields of view in the optical microscope. These data do not take into account incomplete bottom-up etching, which cannot be seen optically. A data point is not given for the free-standing sample after 248 h in 1 M KOH(aq) because no unetched wires were observed.

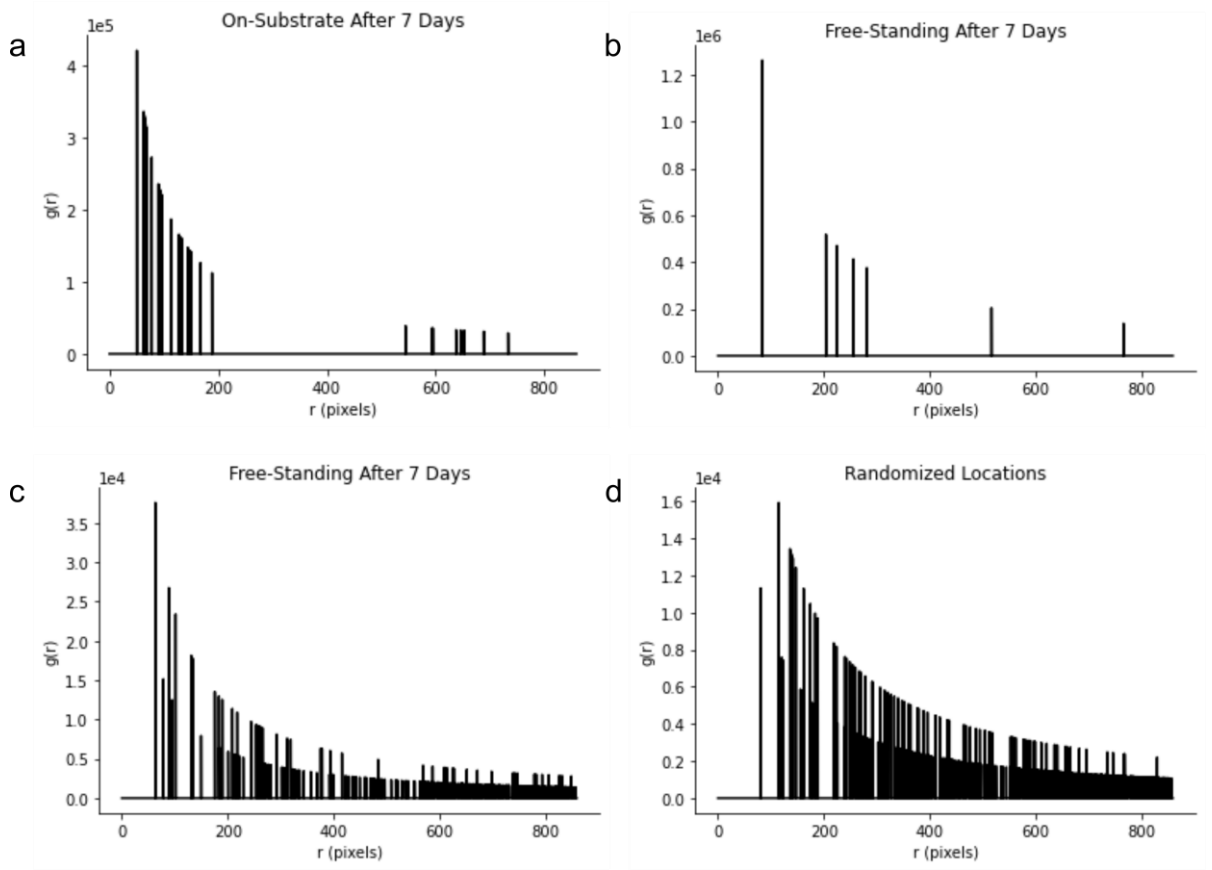

Figure S2. Pair distribution functions (PDF's) for etched wires identified in optical images for an on-sample (a) and free-standing sample (b) after 7 days in 1 M KOH(aq). Panel (c) shows the PDF for the free-standing image with the most optically visible etched wires, compared to a random distribution of the same number of wires in (d). The optical images used to generate panels (b) and (c) were taken from different locations on the same sample.

The analysis in Fig S2 shows that the top-down etching visible under the optical microscope approaches a random distribution, whereas the top-down to bottom-up corrosion seen in the on-substrate samples results in growing clusters of etched wires.