

I. Materials and Methods:

All chemicals and reagents were purchased from Sigma-Aldrich and used as received unless noted otherwise.

Molten salt electrolysis. Different ratios of CaSiO₃, CaO (Na₂O), CaCl₂ (NaCl, MgCl₂) were added into a cylindrical alumina crucible (inner diameter: 4 cm, height: 15 cm) and heated to 200 °C for 24 h in a vacuum oven to remove moisture. Then, the alumina tube was transferred to a sealed fused silica reactor, which was heated by a tube furnace and under a continuous argon flow to the desired temperatures (850 °C, 700 °C, or 650 °C) for electrolysis (**Figure 1**). Two graphite rods (d = 3 mm) serve as the anode and cathode, respectively. Constant-voltage electrolysis at 850, 700, 650 °C in various molten salt and CaO (Na₂O) compositions (see **Table S1**) was then carried out at -1.6 V for 3 h. As a comparison, constant-voltage electrolysis was also carried out under -1.8, -2.0 V in some molten salt at their respective temperatures. After electrolysis, the working electrode was pulled out of the melt and allowed to cool down to room temperature in Ar atmosphere. The product was washed with buffered HF (2M), HCl (2M), and the deionized water three times to remove the solidified salts and other impurities, and dried in an oven at 80 °C for 12 h. The complete process is illustrated in a flow chart in **Figure S2**. All of the melts investigated as well as the reaction temperatures, reagent ratios, and product yields are summarized in **Table S1**. We also carried out 3-electrode electrolysis by using silver as reference electrode, and ran these 3-electrode electrolysis in the optimized CaCl₂-NaCl-MgCl₂ melts (2:4:1) with 0.5 g CaO supporting electrolyte at 650 °C under a constant voltage of 1.2 V vs. reference electrode. As shown in **Figure S16**, this reaction also yielded silicon nanowires.

Electrochemical reduction synthesis of Si from SiO₂ powder. An alumina tube crucible (inner diameter: 4 cm, height: 15 cm) containing 1.5 g of SiO₂ and 40 g of CaCl₂ was heated to 200 °C for 24 h in a vacuum oven to remove moisture. Then the alumina tube was setup in the same reactor described above and heated to the desired temperature 850 °C for constant-voltage electrolysis at -1.6 V for 3 h.

Materials characterization. The PXRD data were collected on as-synthesized samples on glass substrates using a Bruker D8 Advance powder X-ray diffractometer with Cu K α radiation. The scanning electron microscopy (SEM) images were collected on a LEO SUPRA 55 VP field-

emission scanning electron microscope operated at 5.0 kV. Energy-dispersive X-ray spectroscopy (EDX) was performed on single NWs transferred onto an aluminum foil using the same SEM equipped with an EDX detector operating at 10.0 kV. The transmission electron microscope (TEM) characterizations were performed using a Tecnai TF-30 microscope operating at an accelerating voltage of 300.0 kV.

Solubility tests. The solubility of CaSiO_3 in molten $\text{CaCl}_2\text{-NaCl}$, $\text{MgCl}_2\text{-NaCl}$, and $\text{CaCl}_2\text{-MgCl}_2\text{-NaCl}$ salts (40 g in total) with 0.5 g of CaO as the supporting electrolyte at different temperatures was measured by a series of static dissolution experiments at 450, 550, 650, and 750 °C. CaSiO_3 powder was pressed into pellets. Each pellet was weighed and then wrapped by foamed copper foil and Ni wire. The initial masses of the CaSiO_3 pellets were denoted as A . The wrapped CaSiO_3 pellets were immersed in the molten salts for 2 h at different temperatures and then taken out from the melt. After being cleaned by distilled water, the residual CaSiO_3 was weighed again, and the masses were denoted as B . Correspondingly, the solubility (S) of CaSiO_3 in the salt at different temperatures was calculated by the following equation:

$$S = \frac{B-A}{40\text{ g}} \times 100\% \quad (8)$$

Lithium-ion battery assembly and measurements. The silicon NWs were used as active materials for lithium batteries and the electrodes were prepared as follows: A 6.5 wt% solution of polyvinylidene difluoride (PVDF) binder in N-Methyl-2-pyrrolidone (NMP) was prepared. A slurry consisting of Si NWs, carbon black, and PVDF in a ratio of 5:3:2 wt% was pasted on a smooth Cu foil (18 μm thickness) and dried at 80 °C in a vacuum oven overnight. The mass loading of the electrode was 1.1 mg cm^{-2} . The electrodes were packed into CR2016-type coin cells in an argon-filled glovebox with Li metal as the counter electrode, 1 M LiPF_6 in EC/DMC (1/1 by volume, BASF) as the electrolyte, and Celgard membrane as the separator. Galvanostatic cycling experiments were performed using a Biologic SP-200 Potentiostat controlled by EC-Lab software.

II. Supplementary Discussion of the Electrochemical Characterizations and Reaction Mechanisms

Electrochemical investigation of different molten salt systems. Figure 2h shows the CV curves of CaSiO₃ electrolysis in different salt systems. Initially, both CV curves of CaCl₂-NaCl and CaCl₂-MgCl₂ systems at 700 °C exhibited small A1/C1 redox peaks and sharp A2/C2 peaks, which suggest that SiO₃²⁻ reduction (reaction 4) is mostly prohibited and the formation and redissolution of Ca dominates. The low solubility of CaSiO₃ likely leads to slow reaction rate and more side reaction of Ca formation, which results in a liquid Ca layer deposited on the graphite cathode detrimental to the electrochemical reduction of SiO₃. However, the optimized ternary molten salts display CV curves with much higher A1/C1 peak current of over 120 mA, which is almost 3 times higher than that of other two systems, indicating the most favorable reaction kinetics. This is also consistent with the results of current-time curves at a constant voltage of -1.6 V when different electrolytes were used (Figure 2j).

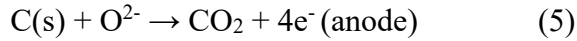
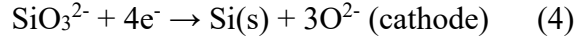
Investigation of reaction time. The CV curves at different reaction times were acquired (Figure S8). After electrolysis for 1 h, the A1/C1 peaks became much more pronounced, compare to the peaks before electrolysis. In addition, large overpotential was also observed, which favors reaction 4 and facilitates the dissolution of CaO and CaSiO₃. This is believed to originate from the activation process, during which due to the high cathodic overpotential, more ionized O²⁻ was generated in the melt through reaction 4. The CV curve barely changed after 1 h, which suggests that the electrolysis process has been stabilized after the initial activation step and steady state O²⁻ migration in the melt was achieved.

Investigation of electrolysis voltage. To determine the proper voltage required for the electrochemical reduction at the highest rate with the purest product, we studied the reaction under various applied constant voltages (Figure 2i). Under -1.6 V, despite the initial polarization, the galvanostatic current was the most stable and remains the highest after 3 h, indicating the most stable Si deposition. Under -1.8 V, the initial current trend was almost the same as that under -1.6 V. However, the current decreased more rapidly after the initial drop. Under a voltage of -2.0 V, the current was higher for the initial 0.5 h, but then slowly approached ~ -4 mA, indicating the reaction has stopped. -1.6 V is the optimal voltage for the stable electrodeposition of Si in CaCl₂-NaCl-MgCl₂ melts with the supporting electrolyte of CaO at 650 °C.

Calculation of Coulombic efficiency of the electrolysis. The electrolytic yield is generally about 70% for optimized reaction conditions. For example, if we take the electrolysis reaction using CaO supporting electrolyte and CaCl₂-NaCl-MgCl₂ melts at 650 °C at 1.6 V as an example, by integrating the I-t curve of the reaction over the 4 h reaction time, we can calculate the Q_{input} of the sample:

$$Q_{\text{input}} = 1230 \text{ C}$$

And due to the reaction (4) and (5) in page 2, we know that 4 electron is needed to produce 1 Si:



With the product yield of 68 mg for this specific reaction run, we can calculate the Q_{output} through the equation below:

$$Q_{\text{output}} = \frac{68 \times 10^{-3}}{28} \times 4 \times 96480 = 909 \text{ C}$$

Then we can calculate the Coulombic Efficiency through the following equation:

$$\text{Coulombic efficiency} = \frac{Q_{\text{output}}}{Q_{\text{input}}} = \frac{909}{1230} = 73\%$$

III. Supplementary figures and figure captions:

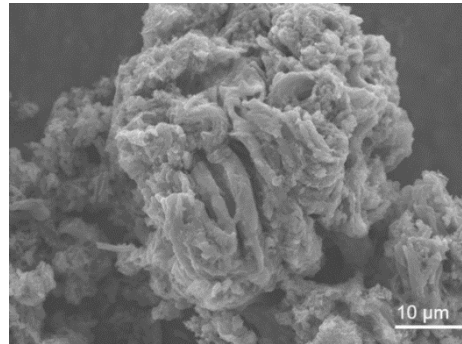


Figure S1. SEM image of the final product using SiO₂ powder as the precursor in the CaCl₂ salt after a 3 h electrolysis under 1.6 V at 850 °C.

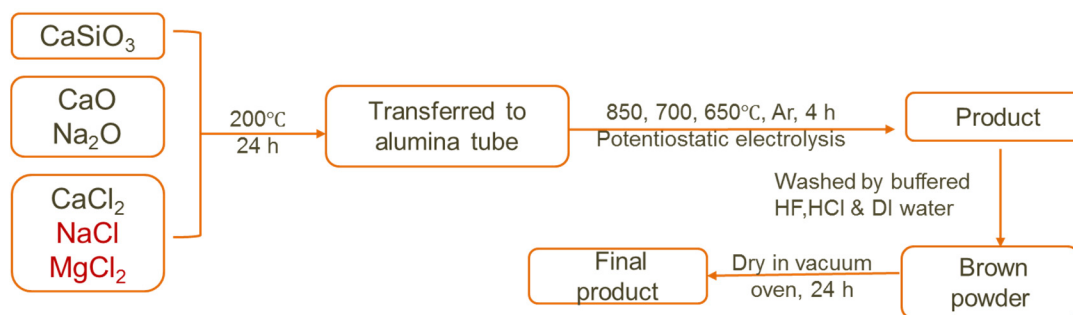


Figure S2. Schematic process flow to prepare the molten salts and electrochemical reduction and the post-reaction treatment to separate the final silicon product from the solidified molten salts.



Figure S3. Photographs of the silicon product from the electrolysis reaction using CaSiO_3 + CaCl_2 salts under 850°C after a 3 h electrolysis under 1.6 V (reaction 1 in Table S1).

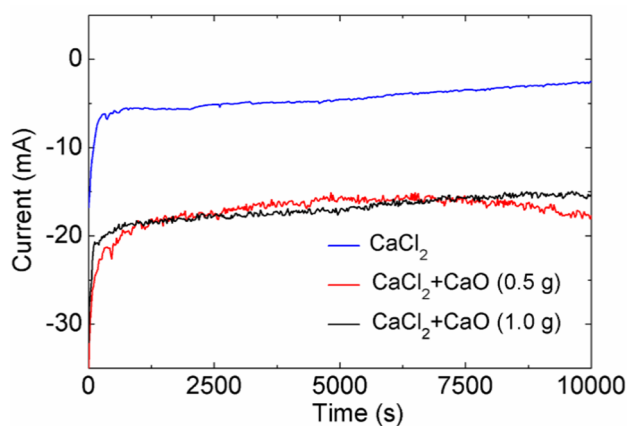


Figure S4. Current-time curves of electrolysis reactions in CaCl_2 - CaO salts (0, 0.5 and 1.0 g, respectively) at 850°C under a constant voltage of -1.6 V for 3h.

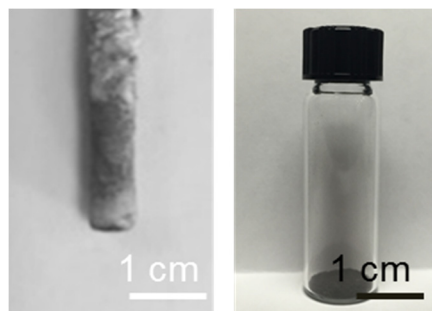


Figure S5. Photographs of the silicon product from the electrolysis reaction using $\text{CaSiO}_3 + \text{CaCl}_2 + \text{NaCl}$ salts at 700°C after a 3 h electrolysis under 1.6 V.

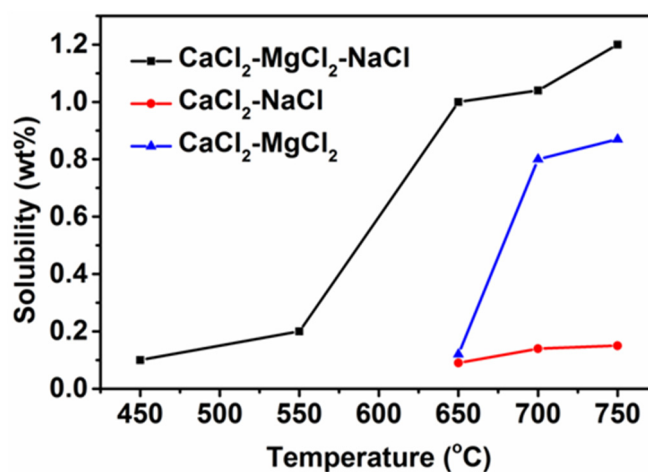


Figure S6. Solubility-temperature curves of CaSiO_3 in molten $\text{CaCl}_2\text{-NaCl}$, $\text{CaCl}_2\text{-MgCl}_2$ and $\text{CaCl}_2\text{-MgCl}_2\text{-NaCl}$ eutectics.

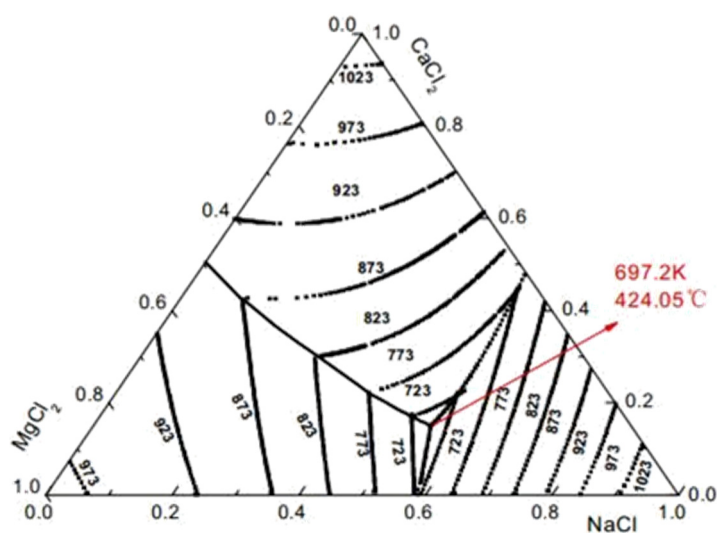


Figure S7. Phase diagram of the ternary molten salt system (NaCl-CaCl₂-MgCl₂) (reprinted with permission from *Applied Energy* 2015, 156, 306).

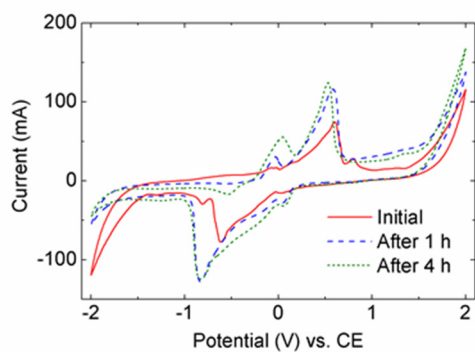


Figure S8. CV curves at different reaction times for electrolysis reactions in the optimized CaCl₂-NaCl-MgCl₂ melts (2:4:1) at -1.6 V.

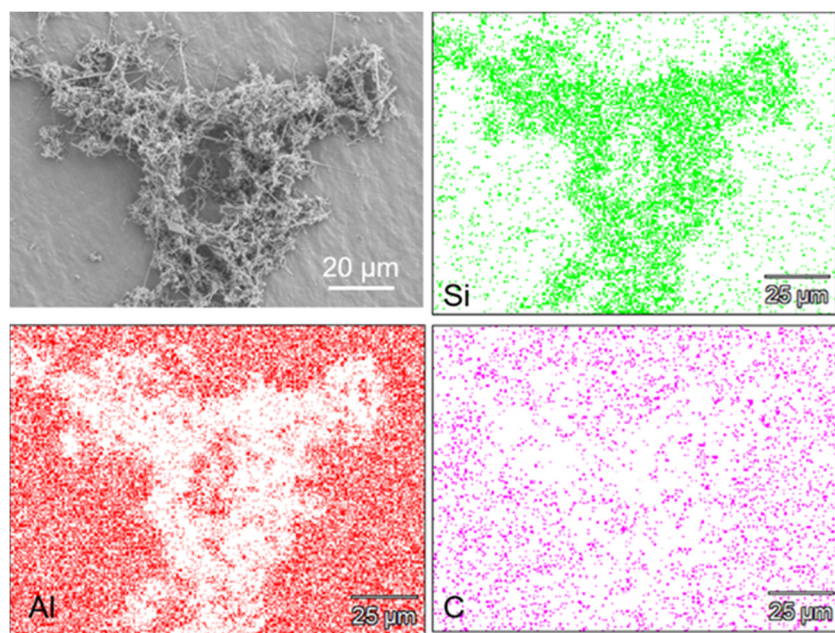


Figure S9. EDS mapping of the silicon nanowire product by using CaCl₂, NaCl and MgCl₂ ternary molten salts with CaO as supporting electrolyte after 3 h electrolysis under -1.6 V.

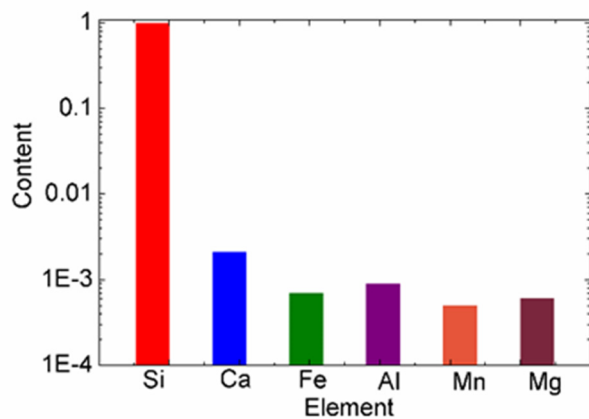


Figure S10. ICP-AES results of the silicon nanowire product in log scale.

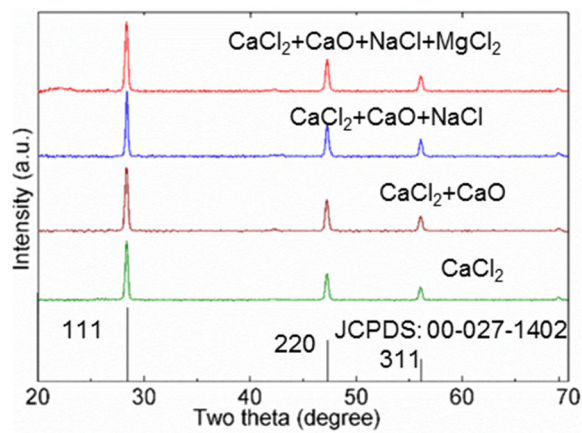


Figure S11. XRD patterns of the final products made using different molten salt systems under a constant voltage of 1.6 V electrolysis reaction, in comparison with the standard PXR pattern of silicon (JCPDS: 00-027-1402).

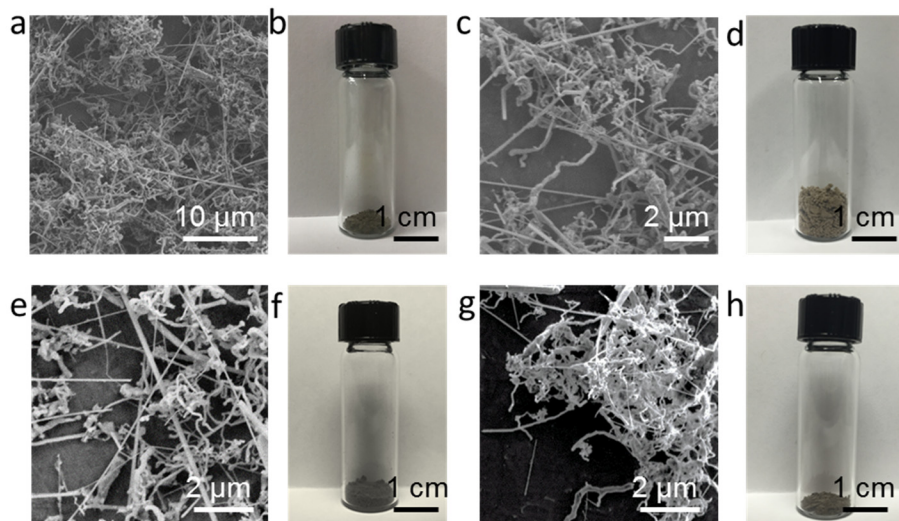


Figure S12. a), c), e), g) SEM images of the electrolysis products using $\text{CaCl}_2+\text{NaCl}+\text{MgCl}_2$ ternary molten salt with CaO (0.5 g) as supporting electrolyte after 3 h electrolysis under -1.5, -1.6, -1.8, and -2.0 V (reaction 35, 29, 33, and 34 in Table S1), respectively. b), d), f), h) Photographs of the electrolysis products using $\text{CaCl}_2+\text{NaCl}+\text{MgCl}_2$ ternary molten salt with CaO (0.5 g) as supporting electrolyte after 3 h electrolysis under -1.5, -1.6, -1.8, and -2.0 V, respectively.

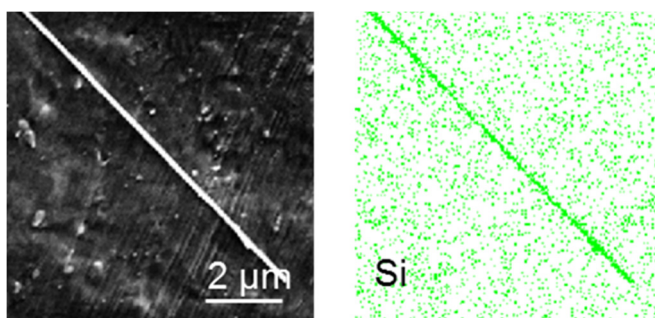


Figure S13. EDS mapping of the Si NW product.

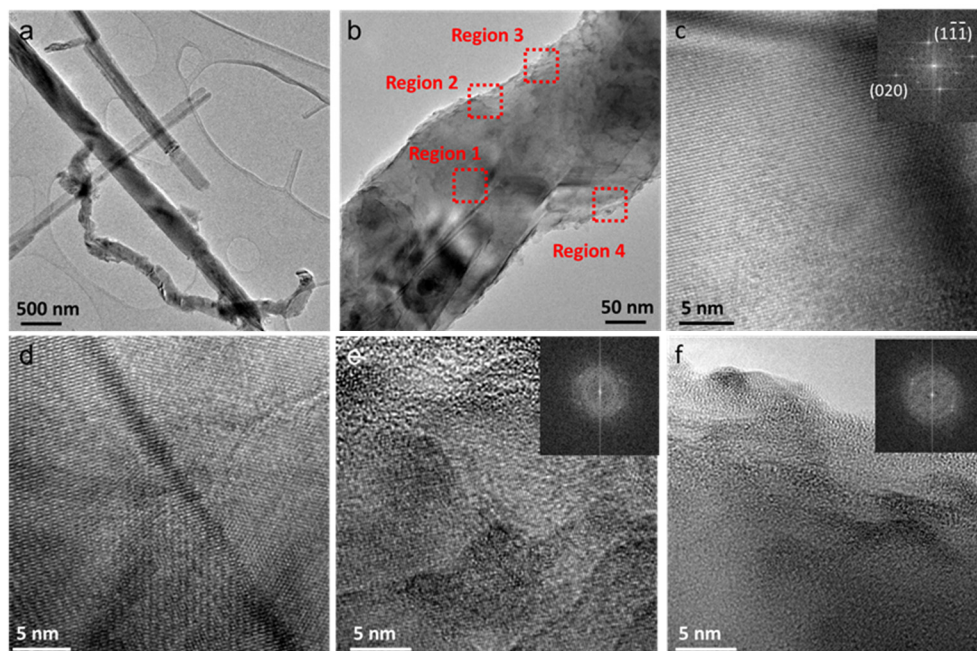


Figure S14. a, b) Additional TEM images of the Si nanowire product highlighting the more curly nanowires made under optimized reaction conditions. c-f) HRTEM images of region 1-4 from panel b, respectively. The HRTEM image of Region 1 shows good crystallinity. The HRTEM image of Region 2 shows the interface of a clear boundary. The boundaries of the nanodomains show rather poor crystallinity compared with the straight one. Thus, we believe that the curved nanowires are polycrystalline.

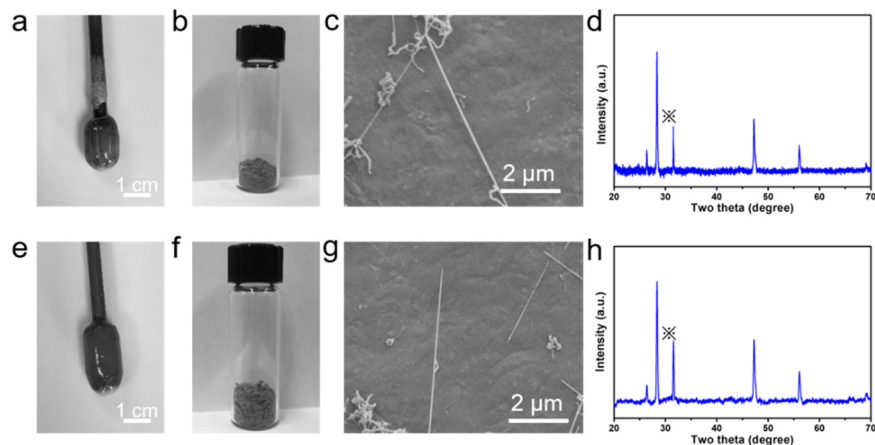


Figure S15. Photographs, SEM and XRD of the products after electrolysis reactions using a), b), c), d) molten salt: $\text{CaSiO}_3 + \text{CaCl}_2 + \text{NaCl} + \text{MgCl}_2 + \text{CaO}$ (0.4 g) + Na_2O (0.11 g) (reaction 42 in Table S1). e), f), g), h); and $\text{CaSiO}_3 + \text{CaCl}_2 + \text{NaCl} + \text{MgCl}_2 + \text{CaO}$ (0.3 g) + Na_2O (0.22 g) (reaction 43 in Table S1).

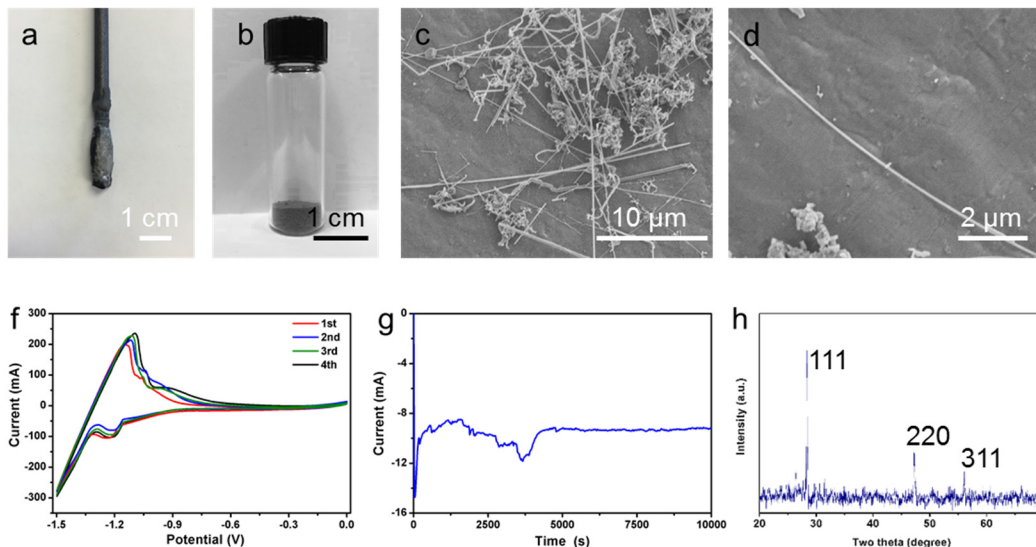


Figure S16. a, b) Photographs of the silicon product from the 3-electrode electrolysis using a silver reference electrode in the optimized $\text{CaCl}_2\text{-NaCl-MgCl}_2$ melts (2:4:1) after electrolysis under 1.2 V vs. reference electrode. c, d) SEM images of the Si nanowires at different scales. e) CV curves in three electrode system at different cycle times. f) I-t curve in three electrode system. g) PXRD of the Si nanowire product.

Table S1. A summary of the details of the reaction conditions (reaction temperature, electrolysis voltage) using different molten salts (CaCl_2 , NaCl , MgCl_2) and supporting electrolytes (CaO , Na_2O) in various ratios and the yield of the silicon product after a 3h electrolysis reaction.

	CaSiO_3	CaO	CaCl_2	NaCl	MgCl_2	Na_2O	Temp ($^\circ\text{C}$)	Voltage (V)	Product Mass (mg)	Salts
1	1.5	--*	40	--	--	--	900	-1.6	55	CaCl_2
2	1.5	0.5	40	--	--	--	850	-1.6	135	$\text{CaO}+$
3	1.5	0.5	40	--	--	--	850	-1.8	80	CaCl_2
4	1.5	0.5	40	--	--	--	850	-2.0	50	
5	1.5	0.5	35	5	--	--	800	-1.6	5	$\text{CaO}+$
6	1.5	0.5	30	10	--	--	700	-1.6	10	$\text{CaCl}_2+\text{NaCl}$
7	1.5	0.5	30	10	--	--	700	-1.8	10	
8	1.5	0.5	30	10	--	--	700	-2.0	10	
9	1.5	0.5	30	10	--	--	700	-2.2	15	
10	1.5	0.5	25	15	--	--	700	-1.6	10	

11	1.5	0.5	20	20	--	--	700	-1.6	--	
12	1.5	0.5	15	25	--	--	700	-1.6	--	CaO+
13	1.5	0.5	10	30	--	--	650	-1.6	--	CaCl ₂ +MgCl ₂
14	1.5	0.5	--	40	--	--	600	-1.6	--	
15	1.5	0.5	35	--	5	--	750	-1.6	40	
16	1.5	0.5	30	--	10	--	700	-1.6	60	
17	1.5	0.5	25	--	15	--	700	-1.6	53	
18	1.5	0.5	20	--	20	--	700	-1.6	10	
19	1.5	0.5	15	--	25	--	700	-1.6	--	
20	1.5	0.5	10	--	30	--	700	-1.6	--	
21	1.5	0.5	--	--	40	--	700	-1.6	--	
22	1.5	0.5	15	15	15	--	650	-1.6	--	CaO+
23	1.5	0.5	20	10	10	--	650	-1.6	35	CaCl ₂ +NaCl+
24	1.5	0.5	24	8	8	--	650	-1.6	40	MgCl ₂
25	1.5	0.5	16	16	8	--	650	-1.6	--	
26	1.5	0.5	24	16	8	--	650	-1.6	55	
27	1.5	0.5	24	16	6	--	650	-1.6	20	
28	1.5	0.5	24	11	6	--	650	-1.6	35	
29	1.5	0.5	24	12	6	--	650	-1.6	75	
30	1.5	0.5	24	13	6	--	650	-1.6	45	
31	1.5	0.5	24	12	5	--	650	-1.6	15	
32	1.5	0.5	24	12	4	--	650	-1.6	14	
33	1.5	0.5	24	12	6	--	650	-1.8	45	
34	1.5	0.5	24	12	6	--	650	-2.0	20	
35	1.5	0.5	24	12	6	--	650	-1.5	12	
36	1.5	0.5	24	12	8	--	650	-1.6	12	
37	1.5	0.5	16	8	16	--	650	-1.6	--	
38	1.5	0.5	18	6	12	--	650	-1.6	--	
39	1.5	0.5	24	6	12	--	650	-1.6	--	
40	1.5	0.5	10	10	20	--	650	-1.6	--	
41	1.5	0.5	10	20	10	--	650	-1.6	--	
42	1.5	0.4	24	12	6	0.11	650	-1.6	80	CaO+
43	1.5	0.3	24	12	6	0.22	650	-1.6	75	Na ₂ O+CaCl ₂ +
44	1.5	0.2	24	12	6	0.33	650	-1.6	45	NaCl+MgCl ₂
45	1.5	0.1	24	12	6	0.44	650	-1.6	23	
46	1.5	--	24	12	6	0.55	650	-1.6	15	

*means that the salt is not added or no silicon is produced.