Supplementary Data

This Supplementary Information presents some methodological elements and supplementary results that support the main manuscript.

Sustainable chemical process to recycle end-of-life silicon solar cells

Rong Deng[a*], Pablo Ribeiro Dias[a,b], Marina Monteiro Lunardi[a], and Jingjia Ji[a]

[a] *School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW, Australia*
[b] *LACOR, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil*

Supplementary 1: The impact of maximum voltage and current density on energy efficiency during reverse electroplating.

Cathodic current efficiency (%) is defined as the ratio between the amount of electricity used for the formation of the cathodic deposit and the total amount of electricity consumed in the process. Energy consumption indicates the amount of energy used for the formation of one kg of silver deposits on the cathode [1].

$$Specific\ cathodic\ efficiency = \frac{\Delta m_{Ag}}{\int c \cdot I \cdot t}$$

$$Energy\ consumption = \frac{\Delta m_{Ag}}{\int c \cdot I \cdot V \cdot t}$$

Δm_{Ag} is the weight change on the cathode, which indicates the mass of the new silver deposits. c is the electrochemical equivalent of metals relevant to solar cell metallisation, which equals to 4.0245 g/Ah for silver[2]. I is the spontaneously current, V is the spontaneously voltage, and t is the time in second.

Higher maximum voltage settings increased the silver removal yield, but also increased the energy consumption and specific cathodic efficiency, as shown in Figure S1, the energy consumption increased from 2 kWh/kg to 3.5 kWh/kg while increasing maximum voltage setting from 6V to 30V. Higher current density negatively significantly increases the energy consumption, from 2 kWh/kg to 26.5 kWh/kg at 3mA/cm^2 and 40 mA/cm^2 respectively.

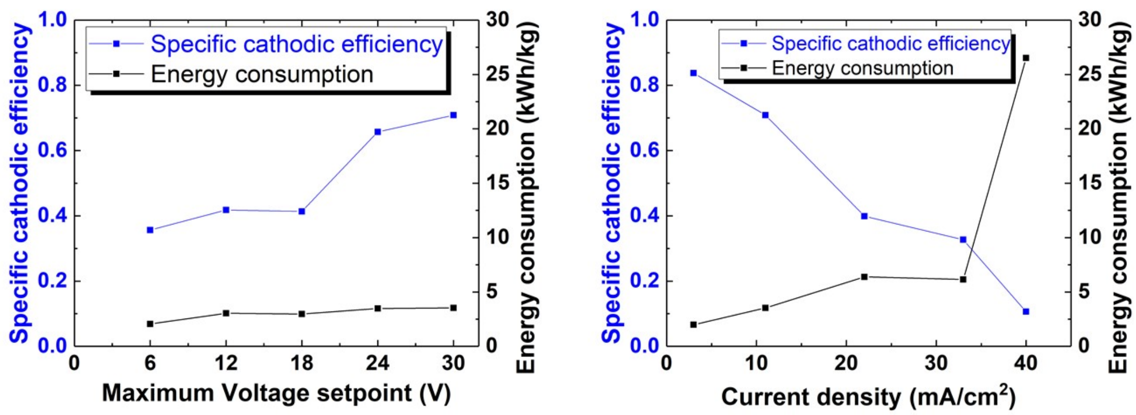

Figure S1 The impact of maximum voltage setpoint and current density on energy consumption during reverse electroplating.

Supplementary 2: determining the purity of recovered silver.

Silver powder was scrapped from the cathode silver coil then dissolved in 4ml 30% $_{w/w}$ heated HNO_3 at 80-90 °C for 3 hours for ICP measurement. The measurement was conducted by ICP-MS (Perkin Elmer, NexION 300D with Universal cell technology) with Discrete Dynode detector. The result was analysed by Syngistix for ICP-MS software. The technique used was Quadrupole Mass Spectrometry from Ions generated by Inductively Coupled plasma. The detection limits (approx.) was 0.5 ppm. The instrument is calibrated using a single solution containing few elements of different mass range, semi-quantitative analysis for 70-73 elements is performed. Semi-quantitative analysis provides a fingerprint of the elements present in a sample and the approximate concentrations of each element. The full result is shown in Table S1, those concentration below the detection limit were excluded. The sum of all impurities is equal to 494 mg/kg, or 0.049% by weight. A 50% uncertainty range was assumed (an extreme assumption), so that the final impurity concentration was approximately 0.1% by weight, implying the silver purity exceeds 99.90%.

Table S1 Semi-quantitative ICP-MS analysis of recovered silver.

Element	mg/kg (ppm)	Element	mg/kg (ppm)
Ag	Saturated		
Al	5.73	Na	7.5
Au	1.72	Ni	5.16
Ba	3.08	Pb	59.9
Bi	9.52	Pd	0.1
Cd	0.07	Rb	0.1
Cu	54.1	Rh	0.06
Hg	0.84	Sn	2.77
Ho	0.00	Sr	0.1
I	1.89	Te	198.0
K	114	Ti	0.3
Li	0.21	V	0.97
Mg	0.9	W	5.18
Mn	0.1	Zn	17.66
Mo	3.8	Zr	0.09
Total, impurities (ppm)		**494.21**	
Impurities, %		**0.049420608**	
50% uncertainty		**0.10**	
Calculated Ag, %		**99.90**	

Supplementary 3: composition analysis of the residue after alkaline etching.

Figure S2(a) shows the tank during alkaline etching. Some insoluble residues dropped at the bottom of the tank. Then, the residue was collected with a fiberglass filter (Figure S2(b)), rinsed three times and dried to prepare samples for SEM, EDX and XPS measurement. The SEM and EDX are shown in the main manuscript. XPS measurements were conducted by professional staff at UNSW Solar Industrial Research Facility, the result is shown in Figure S3.

Figure S2 Photos of (a) alkaline etching reaction and (b) collected insoluble residues.

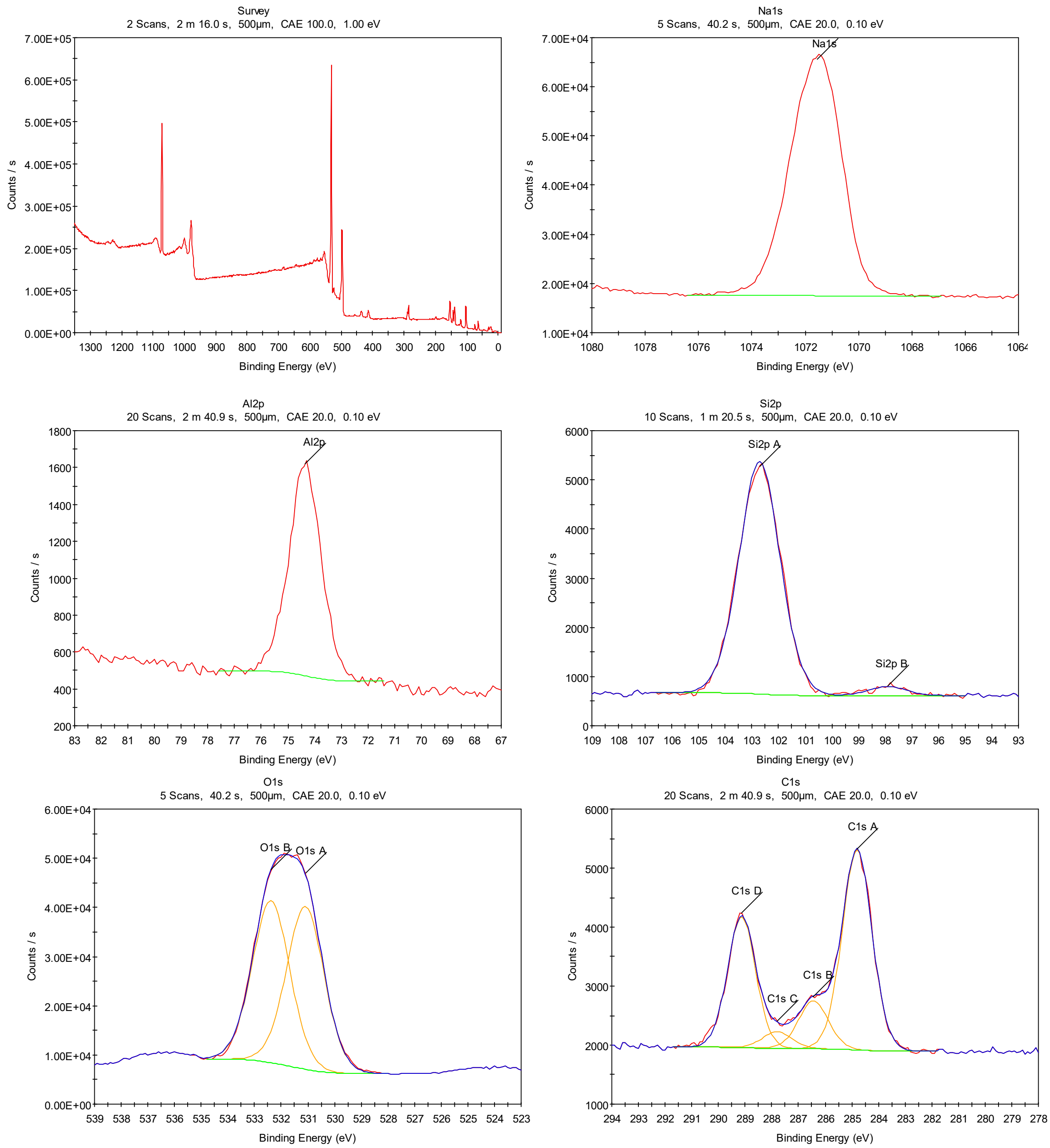

Figure S3 XPS results of residuals. It indicates the composition of this Sodium Aluminosilicate is $Na_{16.9}Al_{3.8}\,Si_{13.1}O_{52.}$

Sodium Aluminosilicate is manufactured with a range of compositions it is not strictly a chemical compound with a fixed stoichiometry [1]. It is insoluble in water, alcohol, organic solvents; partially soluble in strong acids and in alkali hydroxides at 80-100 °C [3].

Supplementary 4 – Life cycle inventory

The inventory data was collected from experiments considering the input and output flows (Table S2) and from the Ecoinvent database (used flow names can be found in Table S3). The OpenLCA software was used to calculate the impacts. During experiment, the HNO_3 and NaOH were used to process multiple batches until the agents needed to be replaced and counted the treated mass. The chemical consumption was scaled by the treated mass to 1000 g solar cells. When the chemical concentration dropped to a certain level the reaction stopped, and the unreacted chemicals were considered as chemical wastes, the flow used in Ecoinvent database was "treatment, PV cell production effluent, to wastewater treatment, class 3" (Table S4). For electricity, we considered the DC power required for electrodeposition, electricity for heating, electricity for ventilation and stirring during the chemical reaction, electricity for rinsing and drying the recovered material, based on the power rating of the experimental tools. The consumption of the electrolyte is not shown in the table. This is because the electrolyte can be reused continuously, so we assume the chemical consumption of the electrolyte is zero. The only input during reverse electroplating is the electricity.

We considered three lab-scale recycling processes Table S2 shows the summary of input and output flows, the data was estimated from our experiments and the experiment conducted by Eshraghi et al. [4] and Huang et al. [5]. Table S3 shows the flow names used in Ecoinvent database.

Scenario 1: conventional solar cell recycling this study (Eshraghi *et al.* [4] and Huang *et al.* [5] 's work)

- Step 1 (Eshraghi): KOH etching to remove Al.
- Step 2 (Eshraghi): HNO_3 etching to dissolve Ag and get 2N Si.
- Step 3 (Hunag): Electrowinning recycle Ag.

Scenario 2: baseline process developed in this work

- Step 1: Reverse plating recycle Ag
  HNO_3 dissolve remaining Ag
- Step 2: NaOH etching to recover 4N Si.

Scenario 3: advanced process developed in this work (with further HNA etching to purify silicon)

- Step 1: Reverse plating recycle Ag
  HNO_3 dissolve remaining Ag
- Step 2: NaOH etching to recover 4N Si.
- Step 3: HNA etching to purify Si (5N).

Table S2 Input and outflow flows for all four scenarios analysed.

Inventory (Functional unit = 1kg solar cell.)					
Scenario 1 – conventional (Eshraghi + Huang)		Step	Flow	Quantity	Unit
	Input	1 - Etch Al	KOH (8M)	896	g
			Electricity	0.63	kWh
		2 - Dissolve Ag	HNO3 (8M)	630	g
			Electricity	1.31	kWh
		3 - Recover Ag by electrowinning	Electricity	0.49	kWh
	Output	1 - Recycle Ag	Up to 74% Ag	10.73	g
		2 - Recycle Si	Up to 99% Si	918	g
		Chemical waste	Waste (chemical)	1372	g
Scenario 2 – baseline. (this study)		Step	Flow	Quantity	Unit
	Input	Reverse electroplating	HNO3	31.5	g
			Electricity	1.17	kWh
		Alkline etching	NaOH	580	g
			Electricity	0.76	kWh
		HNA etching	HNO3	1080	g

			HF	136	g
			CH3COOH	79.4	g
			Electricity	0.22	kWh
	Output	Output	Silver	13.78	g
			Silicon	924	g
			Chemical waste	1766	g
Scenario 3 – Advanced (this study)		Step	Flow	Quantity	Unit
	Input	1 - Recycle Ag	HNO3	31.5	g
			Electricity	1.17	kWh
		2 - Recycle Al	NaOH	580	g
			Electricity	0.76	kWh
	Output	1 - Recycle Ag	Silver	13.78	g
		3 - Recycle Si	Silicon	918	g
		Chemical waste	Chemical waste	532	g

Table S3 Flow names used in Ecoinvent database.

Flow names - Ecoinvent database	
Data from OpenLCA	Flow
KOH	potassium hydroxide, at regional storage
Electricity	electricity mix - China
HNO3	nitric acid, 50% in H2O, at plant
Ag	silver, from combined metal production, at beneficiation + silver, secondary, at precious metal refinery
Si	MG-silicon, at plant
NaOH	sodium hydroxide, 50% in H2O, production mix, at plant
HF	hydrogen fluoride, at plant
CH3COOH	acetic acid, 98% in H2O, at plant
Al	aluminium product manufacturing, average metal working

Table S4 Chemical sludge estimation. Ecoinvent flow: treatment, PV cell production effluent, to wastewater treatment, class 3.

Waste		Quantity	Unit
Scenario 1	Unreacted HNO3	617	g
	Unreacted NaOH	755	g
Scenario 2	Unreacted HNO3	30.9	g
	Unreacted NaOH	501	g
Scenario 3	Unreacted HNO3	1090	g
	Unreacted HF	95.9	g
	Unreacted CH3COOH	79.4	g
	Unreacted NaOH	501	g

Supplementary 5: Life cycle impact assessment full results

Table S5 shows life cycle impact assessment result for selected 10 mid-point categories; and Table S6 shows the results in other 8 categories that were not analysed in the main manuscript. The results were calculated using methodology detailed in the main manuscript and life cycle inventory detailed in Table S2, Table S3 and Table S4.

Table S5 Life cycle impact assessment of three different lab-scale solar cell recycling processes for 10 categories analysed in the main manuscript.

Inventory		climate change kg CO_2-Eq	fossil depletion kg oil-Eq	freshwater ecotoxicity kg 1,4-DCB-Eq	human toxicity kg 1,4-DCB-Eq	marine ecotoxicity kg 1,4-DCB-Eq	marine eutrophication kg N-Eq	ozone depletion kg CFC-11-Eq	particulate matter formation kg PM10-Eq	terrestrial acidification kg SO_2-Eq	water depletion m3
1-Conventional	HNO_3/HF	2.00E+00	1.90E-01	1.51E-01	3.52E-03	1.52E-03	6.53E-08	1.64E-03	6.80E-03	4.60E-04	1.28E-04
	Electricity	2.79E+00	5.83E-01	3.41E-01	8.39E-03	3.52E-03	1.59E-08	7.59E-03	2.43E-02	6.57E-03	7.76E-05
	NaOH/KOH	1.71E+00	5.55E-01	8.33E-01	1.96E-02	1.36E-03	1.41E-07	2.01E-03	6.00E-03	1.16E-02	9.52E-04
	Avoided primary Si	-4.58E+00	-1.50E+00	-9.31E-01	-2.14E-02	-5.40E-03	-2.96E-07	-7.39E-03	-2.34E-02	-9.30E-03	-3.89E-04
	Avoided primary Ag	-6.63E-01	-1.67E-01	-2.50E+00	-4.40E-02	-1.09E-02	-5.74E-08	-8.60E-03	-2.76E-02	-1.56E-02	-7.27E-03
	Chemical sludge	2.25E+00	2.54E-01	1.11E+00	1.89E-02	1.77E-03	3.83E-07	2.43E-03	6.64E-03	1.61E-02	8.96E-04
2-Baseline	HNO_3/HF	1.00E-01	9.50E-03	7.56E-03	1.76E-04	7.62E-05	3.26E-09	8.21E-05	3.40E-04	2.30E-05	6.38E-06
	Electricity	2.22E+00	4.64E-01	2.71E-01	6.67E-03	2.80E-03	1.26E-08	6.04E-03	1.94E-02	5.22E-03	6.17E-05
	NaOH/KOH	6.36E-01	1.84E-01	6.42E-01	1.10E-02	5.71E-04	3.89E-08	8.98E-04	2.74E-03	4.71E-03	4.06E-04
	Avoided primary Si	-4.58E+00	-1.50E+00	-9.31E-01	-2.14E-02	-5.40E-03	-2.96E-07	-7.39E-03	-2.34E-02	-9.30E-03	-3.89E-04
	Avoided primary Ag	-8.51E-01	-2.15E-01	-3.21E+00	-5.65E-02	-1.39E-02	-7.37E-08	-1.10E-02	-3.54E-02	-2.01E-02	-9.34E-03
	Chemical sludge	8.71E-01	9.83E-02	4.32E-01	7.34E-03	6.87E-04	1.49E-07	9.44E-04	2.58E-03	6.23E-03	3.47E-04
3-Advanced	HNO_3/HF	4.02E+00	5.36E-01	5.90E-01	1.37E-02	3.29E-03	1.65E-07	5.63E-03	2.37E-02	3.56E-03	3.95E-04
	Electricity	2.47E+00	5.17E-01	3.02E-01	7.44E-03	3.12E-03	1.41E-08	6.73E-03	2.16E-02	5.83E-03	6.88E-05
	NaOH/KOH	6.36E-01	1.84E-01	6.42E-01	1.10E-02	5.71E-04	3.89E-08	8.98E-04	2.74E-03	4.71E-03	4.06E-04
	Avoided primary Si	-4.61E+00	-1.51E+00	-9.37E-01	-2.15E-02	-5.44E-03	-2.98E-07	-7.43E-03	-2.36E-02	-9.36E-03	-3.91E-04
	Avoided primary Ag	-8.51E-01	-2.15E-01	-3.21E+00	-5.65E-02	-1.39E-02	-7.37E-08	-1.10E-02	-3.54E-02	-2.01E-02	-9.34E-03
	Chemical sludge	2.89E+00	3.26E-01	1.43E+00	2.44E-02	2.28E-03	4.94E-07	3.13E-03	8.55E-03	2.07E-02	1.15E-03

Table S6 Life cycle impact assessment of three different lab-scale solar cell recycling processes for 8 categories that were not analysed in the main manuscript.

Inventory		agricultural land occupation m2*a	freshwater eutrophication kg P-Eq	ionising radiation kg U235-Eq	metal depletion kg Fe-Eq	natural land transformation m2	photochemical oxidant formation kg NMVOC	terrestrial ecotoxicity kg 1,4-DCB-Eq	urban land occupation m2*a
1-Conventional	HNO_3/HF	2.73E-03	8.72E-05	3.25E-02	4.73E-02	8.84E-05	3.79E-03	6.19E-05	8.91E-04

	Electricity	8.23E-03	3.54E-04	5.70E-02	9.19E-03	6.77E-04	1.07E-02	5.87E-05	2.22E-02
	NaOH/KOH	1.92E-02	1.06E-03	7.70E-01	1.08E-01	1.70E-04	3.87E-03	9.04E-05	1.54E-02
	Avoided primary Si	-2.06E-02	-1.19E-03	-7.12E-01	-7.46E-02	-9.11E-03	-1.85E-02	-8.52E-05	-2.06E-02
	Avoided primary Ag	-4.80E-02	-1.50E-03	-1.25E+00	-3.45E+00	-4.98E-04	-3.18E-02	-5.31E-05	-1.73E-01
	Chemical sludge	1.84E-02	1.31E-03	1.04E+00	2.61E-01	1.77E-04	5.03E-03	9.60E-05	8.67E-03
2-Baseline	HNO3/HF	1.36E-04	4.36E-06	1.63E-03	2.36E-03	4.42E-06	1.90E-04	3.09E-06	4.45E-05
	Electricity	6.54E-03	2.81E-04	4.53E-02	7.31E-03	5.38E-04	8.51E-03	4.66E-05	1.77E-02
	NaOH/KOH	1.09E-02	6.25E-04	4.62E-01	4.92E-02	1.43E-04	1.44E-03	6.51E-05	2.26E-03
	Avoided primary Si	-2.06E-02	-1.19E-03	-7.12E-01	-7.46E-02	-9.11E-03	-1.85E-02	-8.52E-05	-2.06E-02
	Avoided primary Ag	-6.17E-02	-1.93E-03	-1.60E+00	-4.43E+00	-6.39E-04	-4.09E-02	-6.82E-05	-2.22E-01
	Chemical sludge	7.14E-03	5.07E-04	4.04E-01	1.01E-01	6.87E-05	1.95E-03	3.72E-05	3.36E-03
3-Advanced	HNO3/HF	1.21E-02	5.11E-04	2.98E-01	1.47E-01	2.97E-04	9.31E-03	1.58E-04	3.66E-03
	Electricity	7.29E-03	3.13E-04	5.06E-02	8.15E-03	6.00E-04	9.49E-03	5.20E-05	1.97E-02
	NaOH/KOH	1.09E-02	6.25E-04	4.62E-01	4.92E-02	1.43E-04	1.44E-03	6.51E-05	2.26E-03
	Avoided primary Si	-2.07E-02	-1.20E-03	-7.17E-01	-7.51E-02	-9.17E-03	-1.86E-02	-8.57E-05	-2.07E-02
	Avoided primary Ag	-6.17E-02	-1.93E-03	-1.60E+00	-4.43E+00	-6.39E-04	-4.09E-02	-6.82E-05	-2.22E-01
	Chemical sludge	2.37E-02	1.68E-03	1.34E+00	3.36E-01	2.28E-04	6.48E-03	1.24E-04	1.12E-02