SI Appendix

All reactions involved in both traditional Kraft based cycles and the Mn-Na-CO_2 cycle are listed below:

Table S1 Kraft Cycles

Step	Temperature (°C)	Reaction
1	25	2 NaOH(aq)* + CO_2(g) → Na_2CO_3(aq)* + H_2O
2	25	Na_2CO_3(aq)* + $Ca(OH)_2$ (s) → 2 NaOH(aq)* + $CaCO_3$ (s)
3	600 – 900	$CaCO_3$ (s) → CaO (s) + CO_2 (g)
4	100 – 300	CaO (s) + H_2O (g or l) → $Ca(OH)_2$

***All sodium species may be substituted with potassium.**

Table S2 Mn-Na-CO_2 Cycle

Step	Temperature (°C)	Reaction
1	80 – 90	6 $NaMnO_2$ (s) + 3 CO_2 (g) + 6y H_2O (l) → 3 Na_2CO_3 (aq) + 6 $H_XMnO_2 \cdot yH_2O$ (s)
2	850	6 $H_XMnO_2 \cdot yH_2O$ → Mn_3O_4 + 6y H_2O (g) + O_2 (g)
3	850	3 Na_2CO_3 + 2 Mn_3O_4 + H_2O (g) → 6 $NaMnO_2$ + 3 CO_2 (g) + H_2 (g)

Na-Mn-CO_2 Water Splitting Cycle Thermodynamics:

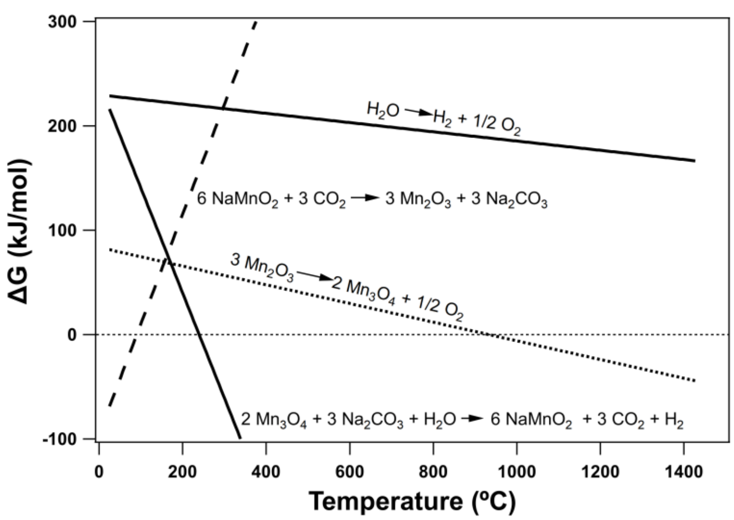

Figure S1. The temperature dependent Gibbs free energy changes of the major reactions of the Mn-Na-CO_2 TWS cycle.

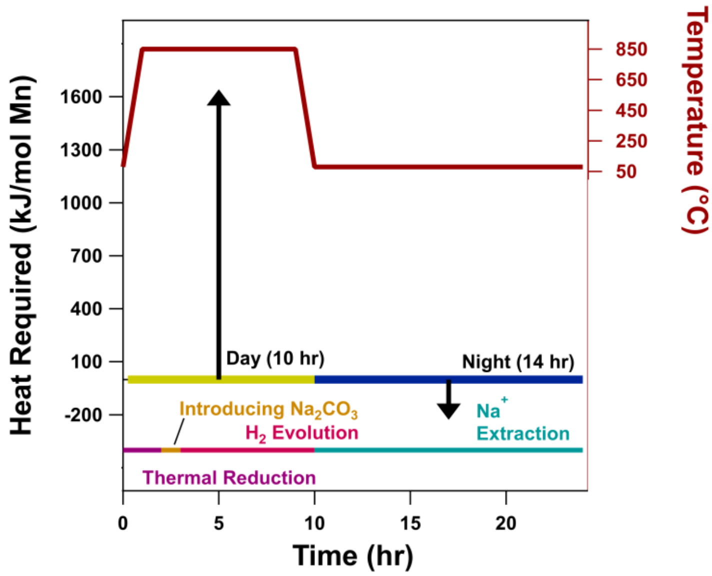

Figure S2. Proposed schedule of the quasi-batch TWS-DAC process.

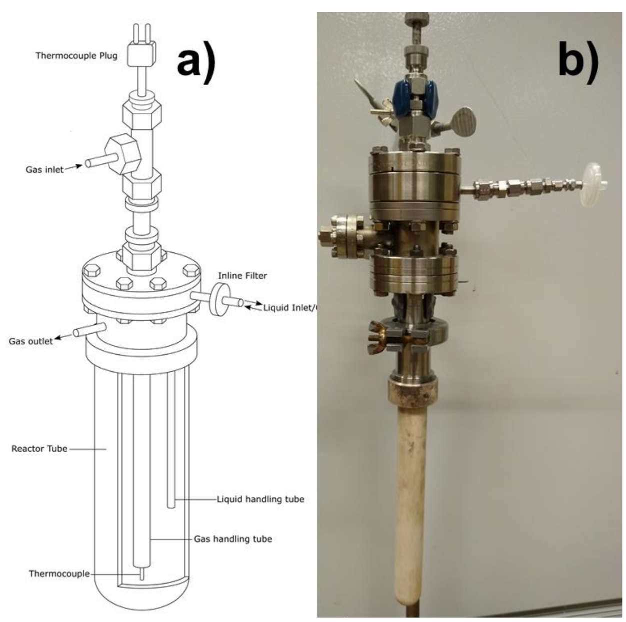

Figure S3. a) Schematic of a) the constructed TWS reactor, and b) Image of the constructed TWS reactor.

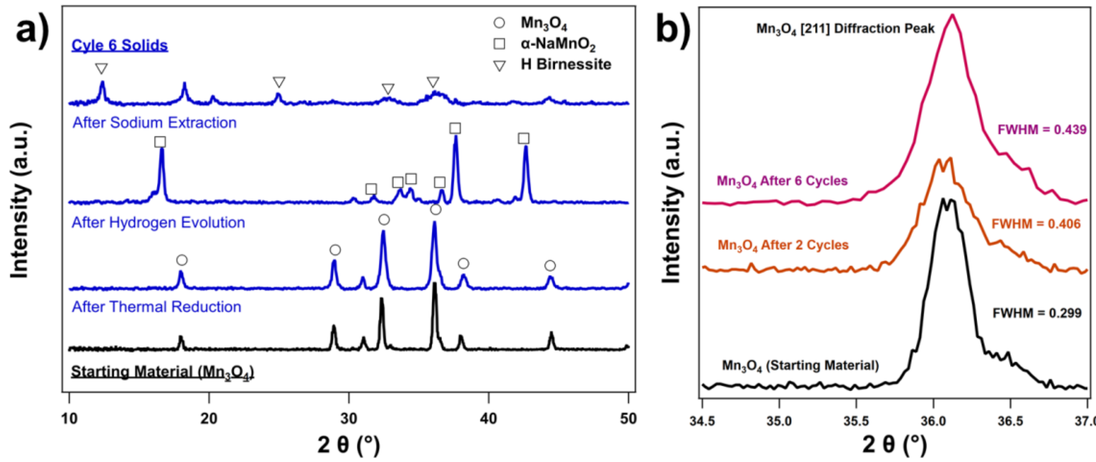

Figure S4. a) XRD patterns of the Na-MnO$_x$ solids after 6 cycles and the starting material (Mn_3O_4) for comparison b) A comparison of the Mn_3O_4 [211] diffraction peak of several manganese solid samples after thermal reduction taken during the 6-cycle experiment.

Technoeconomic Analysis

Our preliminary technoeconomic analysis of our proposed process is detailed below.

Capital Costs

Unit Process	Modelled as:	Purchased Cost(references)
Water Splitting Reactor	230 m^3 Ni alloy vessel w/ 1 ft of foam glass insulation	$715,000[1, 2]
Solar Concentration System	2600 heliostats focused on a central tower	$43,500,000[3]
Solar Updraft Tower	750 m 30 MW updraft tower	$236,000,000[4]
Steam Turbines	5 4000 kW axial turbines	$2,880,000[1]
Air Blowers	23 axial tube fans rated for 100 m^3/s	$625,000[1]
Water Pumps	143 kW recirculation pump and 2 kW feed pump	$213,000[1]

Unit Process	Required Power (kW)	Assumed Efficiency
Water Splitting Reactor	196,000	100%
Solar Concentration System	220,000	90%
Steam Turbines	18,800	40%
Air Blower	30,000	80%
Water Pumps	146	75%

Yearly Revenue/Costs

	Production (tonne/yr)	Selling Price ($/tonne)	Yearly Revenue (Million $/yr)
CO_2 Production	25,100	83 (varied)	1.53

H_2 Production	381	2000	0.762
O_2 Production	3,050	40	0.122

Financial Assumptions

- Lifetime of plant: A plant lifetime of 50 years is assumed; this is optimistic but reasonable as the vast majority of the plant capital is spent on passive solar technologies which require little upkeep.
- The land required for the plant is assumed to be roughly equivalent to that required for the solar harvesting facilities, which are calculated according to similar facilities (3, 4)
- Rate of return: A standard rate of return of 10% is used to calculate all net present values.
- Depreciation: A straight line depreciation model is used to estimate the value of depreciating equipment. It is assumed that the plant at the end of 50 years has no salvage value.
- Non-equipment capital costs: We estimate the costs of equipment installation using a Lang factor of 3 for all equipment priced using chemical engineering economic texts (1,2). Indirect costs are estimated to be an additional 5% of the total direct costs.
- Operation costs: The number of necessary full-time operators is estimated to be ~32 using commonly used relations (1).
- Maintenance: Annual maintenance costs are estimated to be roughly 3% of the total plant cost (5).
- Taxes: Taxes are ignored as successful CO_2 capture plants will likely be given tax credits from the U.S. government.
- Raw Materials: Sodium and manganese are assumed to be replaced once a year in the form of Na_2CO_3 and manganese metallurgical ore. This cost is not plotted in the main text as these materials are inexpensive (Na_2CO_3 sells for 149 $/tonne, manganese ore sells for 9.6 $/tonne of contained manganese) (6) compared to other operating costs and have little effect on the plant's overall profits.

- Electricity: Grid power is assumed to be available to be bought or sold at 0.167 $/kWhr.

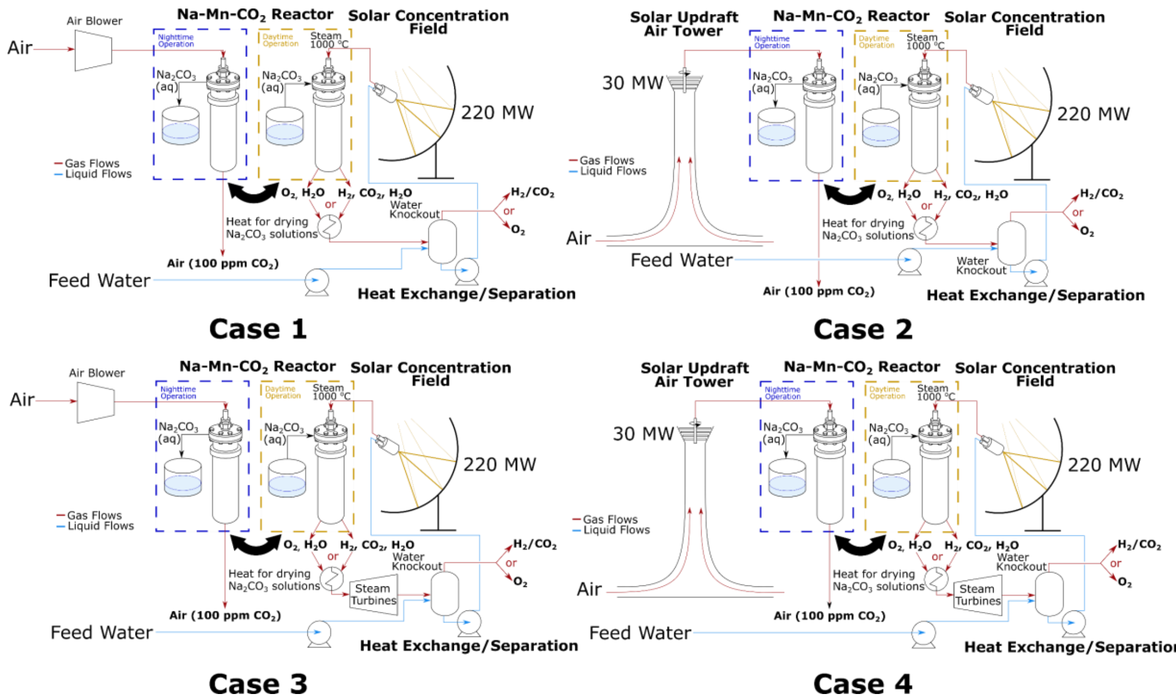

Figure S5. A comparison of the 4 different cases for the technoeconomic analysis.

Comparisons of Cases:

Expenditure	Yearly Cost (Millions of $/yr)
Operations	1.93
Maintenance	
Case 1	1.56
Case 2	1.85
Case 3	1.82
Case 4	2.12
Electricity	
Case 1	18.4
Case 2	-18.2
Case 3	6.93
Case 4	-29.6

Case	Total Capital Investment (Millions of $)	Yearly profit (Millions of $)	NPV (Millions of $)
1	55.0	-15.9	-157
2	302	20.7	-52.6
3	64.0	-5.09	-80.0
4	311	31.5	22.0

Note: All NPV estimates are made using an optimistic CO_2 price of $200/tonne as a baseline value.

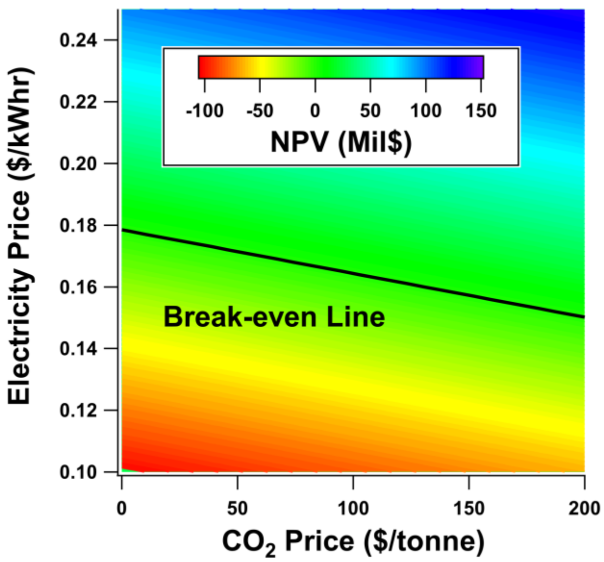

Figure S6. NPV of the process as a function of CO_2 and electricity price.

References:

1. *Analysis, synthesis and design of chemical processes* (Pearson Education, 2008).
2. *Chemical engineering economics* (Springer Science & Business Media, 2012).
3. D. Graf, N. Monnerie, M. Roeb, M. Schmitz, C. Sattler, Economic comparison of solar hydrogen generation by means of thermochemical cycles and electrolysis. *International journal of hydrogen energy* **33**, 4511-4519 (2008).
4. J. Schlaich, R. Bergermann, W. Schiel, G. Weinrebe, Design of commercial solar updraft tower systems—utilization of solar induced convective flows for power generation. *Annu. Rev. Earth. Pl. Sc.* **127**, 117-124 (2005).