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The global potential for converting renewable electricity to negative-CO_2-emissions hydrogen

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The IPCC has assigned a critical role to negative-CO_2-emissions energy in meeting energy and climate goals by the end of the century, with biomass energy plus carbon capture and storage (BECCS) prominently featured. We estimate that methods of combining saline water electrolysis with mineral weathering powered by any source of non-fossil fuel-derived electricity could, on average, increase energy generation and CO_2 removal by >50 times relative to BECCS, at equivalent or lower cost. This electrogeochemistry avoids the need to produce and store concentrated CO_2, instead converting and sequestering CO_2 as already abundant, long-lived forms of ocean alkalinity. Such energy systems could also greatly reduce land and freshwater impacts relative to BECCS, and could also be integrated into conventional energy production to reduce its carbon footprint. Further research is needed to better understand the full range and capacity of the world's negative-emissions options.

It is now recognized that proactive CO_2 removal from the atmosphere (negative CO_2 emissions) will be needed in the likely event that reduction in anthropogenic CO_2 emissions falls short of stabilizing atmospheric CO_2 below levels that will cause unacceptable climate and ocean chemistry impacts[1,2]. In addition to non-energy-producing methods of atmospheric CO_2 removal such as afforestation and direct air capture, recent modelling and policy prominently feature the potential of coupling biomass energy production with carbon capture and storage (BECCS) to effect renewable, negative-CO_2-emissions energy generation[3–5]. Here, at least some of the atmospheric CO_2 initially fixed by land biomass is ultimately captured and stored underground in the course of combusting, gasifying or fermenting that biomass to generate usable energy (electricity, hydrocarbons or H_2)[6]. BECCS is believed to have the potential to remove up to 12 $GtCO_2\,yr^{-1}$ (t = metric ton or tonne) while possibly generating as much a 300 $EJ\,yr^{-1}$ of primary energy[3,4]. This not only reduces CO_2 emissions by substituting for emissions-intensive fossil energy, but also provides a way of removing and sequestering CO_2 from air by preventing biomass carbon from returning to the atmosphere via natural respiration and decomposition.

However, to remove and store gigatonnes of CO_2 per year in this manner would require significantly expanded and/or altered land management, which could impact existing land uses for food, fibre and fuel production, as well as potentially denigrate other ecosystem services[3,4,7,8]. Land impacts could be reduced or alleviated and global negative-emissions energy production potential increased by the use of marine biomass in a BECCS process[9,10], yet potential negative impacts to the marine environment would need to be considered. The CCS component of the process can also be problematic because of its cost and because of the environmental, seismic and storage security concerns of injecting large quantities of such CO_2 underground[8,11–13].

Given these issues and the possibility that the removal of thousands of gigatonnes of CO_2 from the atmosphere may ultimately be required to counter an overshoot in CO_2 emissions[14,15], additional methods of negative-emissions energy production need to be explored. This Article evaluates the application of recently described electrogeochemical methods of converting any non-fossil fuel-derived electricity (hereafter non-fossil electricity) source to a negative-emissions fuel or energy carrier, H_2.

It has been shown that conventional water electrolysis can be modified to (1) concentrate dissolved CO_2 for subsequent use or sequestration or (2) generate excess OH^-/alkalinity in solutions that are highly absorptive of air CO_2 and that convert the CO_2 to long-lived, dissolved or solid mineral bicarbonates and/or carbonates. Central to these processes is the splitting of water at a cathode to form $H_2(g)$ and OH^-, with the generation of $O_2(g)$ (or $Cl_2(g)$) and H^+ at the anode. In one approach[16], the $Na^+ + OH^-$ produced during electrolysis of a NaCl solution (chloralkali process) is used to absorb atmospheric CO_2 and convert it to $NaHCO_3(aq)$ (plus, via chemical equilibrium reactions, a smaller amount of dissolved $Na_2CO_3(aq)$). The H_2 and Cl_2 gases generated are reacted in a fuel cell to produced electricity and HCl (acid). The HCl is subsequently neutralized with alkaline silicate minerals to produced benign/useful Mg and Ca chlorides and silica (Fig. 1a).

In a second approach[17–19], the H^+ produced in the anolyte is directly neutralized with alkaline carbonate or silicate minerals, forcing the remaining electrolyte to accumulate OH^-, which is then used to absorb CO_2 from the atmosphere (Fig. 1b). A third method[20] employs membranes to separate the OH^- (alkaline) and H^+ (acid) solutions produced in compartmentalized water electrolysis, with the latter then used to acidify seawater and thus convert a substantial portion of its resident, dissolved bicarbonate and carbonate to dissolved CO_2 (or carbonic acid, $H^+ + HCO_3^-$). This CO_2 can subsequently be degassed and sequestered from the atmosphere, or, as will be explored here, converted (without degassing) to dissolved seawater bicarbonate (plus carbonate) via spontaneous reaction with solid carbonate minerals[21,22], thus effecting CO_2 sequestration (Fig. 1c; see Methods). Simultaneously, the OH^- stream produced in the preceding electrolysis is also added to seawater to effect air CO_2 capture and storage as dissolved mineral (bi)carbonates in the ocean (Fig. 1c). A related fourth approach[23] uses electrodialysis to

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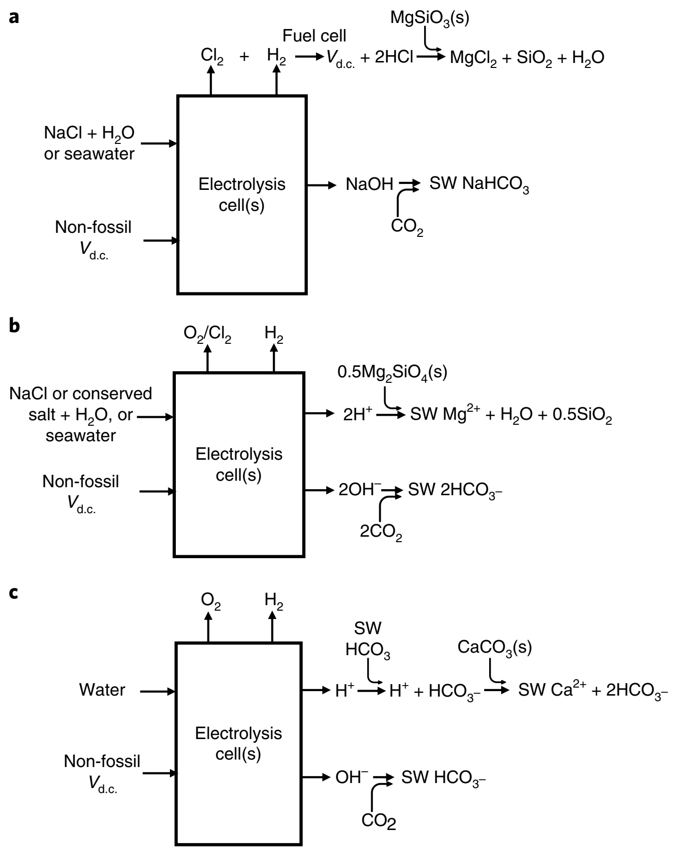

Fig. 1 | Various schemes for electrolytically generating H_2 while consuming CO_2 and transforming it to dissolved mineral bicarbonate. When powered by electricity derived from low- or non-CO_2-emitting energy sources, these schemes are strongly CO_2-emissions negative. **a**, Scheme according to ref. [16]. **b**, Scheme according to refs [18] and [19]. **c**, Scheme according to ref. [20]. SW, seawater; $V_{d.c.}$, direct current electricity.

separate OH^- and H^+ derived from seawater, which can then be used to perform tasks similar to the preceding process. However, in this case water is not split, H_2 is not produced, and thus no energy/fuel production is directly achieved.

Additional methods could include the use of combined solar thermal (T) and photovoltaic (PV) energy to power separate, high-temperature electrolysis of CO_2 and H_2O, yielding the net reaction $CO_2 + H_2O + \text{solar T} + \text{solar PV} \rightarrow C + H_2 + 1.5O_2$ (refs [24–26]). However, it would seem cumbersome to remove and store at gigatonne levels the elemental C that deposits on the cathodes, and the process is also dependent on high-temperature solar heating rather than additional, more diverse and less expensive renewable energy resources.

It is also possible to generate negative-emissions H_2 from biological feedstocks. Here biomass and water can be gasified at high temperature, with the resulting CO oxidized with water to produce CO_2 and H_2. The CO_2 is then captured and stored[6]. The fermentation of biomass can also generate H_2 or hydrocarbon fuels plus semi-concentrated CO_2 (ref. [6]). If this CO_2 is captured and stored, at least some negative emissions is effected. All of these biological methods are, however, ultimately limited by the availability and use of solar energy, land area, water and nutrients for the photosynthetic formation of biomass[3,8].

The following attempts to evaluate the global capacity and cost of producing negative-emissions H_2 (hereafter NE H_2), based on previous estimates of global renewable electricity generation capacities and costs, and based on a representative, reference NE H_2 generation system compiled from available theory, modelling and testing.

H_2 generation and CO_2 removal potentials

Because the net CO_2 removal capacity of NE H_2 is highest when powered by non-fossil electricity, we start by assessing the global capacity of this resource as compiled by the IPCC[27,28] for six categories of renewable energy (Table 1). For the purposes of this Article we use the reported minimum and median or mean values to reflect the more conservative global renewable electricity production ranges that are probably representative of the energy resources available for the application we envision (see Methods). In particular it seems very unlikely that the full, global renewable electricity generation potential of any given type could be exploited and used exclusively for NE H_2. The estimated total potential electrical energy thus ranges from nearly 600 $EJ_e\,yr^{-1}$ to more than 6,000 $EJ_e\,yr^{-1}$, with solar dominating this potential (Table 1). Current global electricity generation is about 90 $EJ_e\,yr^{-1}$ (ref. [29]) and may be 300–600 $EJ_e\,yr^{-1}$ by 2100 (ref. [28]).

The second requirement in our capacity estimations is an understanding of the efficiencies with which the preceding electricity could be converted to H_2 generation and CO_2 removal. Table 2 lists the estimated energy requirements and input/output stoichiometries for three types of NE H_2 process, as derived from theory and the experimentation cited in Fig. 1. From these examples, approximate representative values for a NE H_2 system are listed (Table 2). In these estimates the CO_2 footprint of renewable electricity, <0.014 $Gt\,EJ_e^{-1}$ (ref. [27]) is ignored, because the negative CO_2 emissions per energy input in our representative NE H_2 system, 0.15 $Gt\,EJ_e^{-1}$ (Table 2), is more than 10 times greater than the preceding figure and probably within the uncertainties of the NE H_2 estimates.

Using the global renewable electricity generation potentials (Table 1) and the ratio of H_2 produced or CO_2 removed per EJ_e of energy input (Table 2), the global potentials for energy production as H_2 and for CO_2 removal using NE H_2 systems are then calculated (Table 1, see Methods). The total global energy potential ranges from roughly 300 to 3,000 $EJ_{H2}\,yr^{-1}$, while the global potential for atmospheric CO_2 removal and storage ranges from about 90 to 900 $Gt\,yr^{-1}$ (Table 1). Note that these ranges only reflect ranges in potential renewable electricity availability, which appears to be the denominant source of global estimation variability relative to the much smaller within-parameter ranges listed in Table 2. The ranges in this table are also significantly larger than variations due to (i) the relatively small CO_2 footprint of renewable electricity (above) and (2) the relatively small energy and CO_2 penalties anticipated for mineral extraction, processing and transportation (Supplementary Section 'Minerals'). A fuller consideration of system variability and parameter uncertainties would expand the ranges shown, but would be unlikely to significantly alter the mean quantities implied for each energy source sector. The majority of the preceding global energy generation potential and CO_2 removal capacity comes from the use of solar energy. For perspective, current global H_2 utilization is equivalent to only about 8 $EJ_{H2}\,yr^{-1}$, with demand growing significantly for fuel, refining and energy storage[30]. Anthropogenic CO_2 emissions currently total 41 $Gt\,yr^{-1}$ (ref. [31]).

The $GtCO_2$ removal potential per EJ of energy generation averages 0.30, as derived from the slope of the regression line shown in Fig. 2. This is at least seven times higher than that estimated for BECCS (0.04 $Gt\,EJ^{-1}$; ref. [3]). This suggests that when or where there is a choice between BECCS and NE H_2, the latter could provide greater energy generation per unit CO_2 removed. However, this feature must be weighed against the cost of performing either process in a given location, as well as the desirability of producing H_2 versus electricity. This includes consideration of the demand and infrastructure for a given energy form, which presently greatly favours electricity. That, however, could change under 'hydrogen

Table 1 | Global production potentials and costs of six categories of renewable electricity as reported by the IPCC[27,28], as well as estimated NE H_2 energy production and CO_2 removal potentials and costs when powered by the preceding electricity

Input electricity source	Geo-thermal	Hydro	Ocean	Wind	Biomass	Solar	Total
Global electricity production potential and cost estimates							
High ($EJ_e\,yr^{-1}$)	614	51	169	333	88	5,141	6,395
Low ($EJ_e\,yr^{-1}$)	118	50	7	85	16	315	591
High ($\mathrm{US\$\,kWh_e^{-1}}$)	0.07	0.04	0.21	0.11	0.12	0.29	–
Low ($\mathrm{US\$\,kWh_e^{-1}}$)	0.03	0.01	0.12	0.04	0.02	0.07	–
Global NE H_2 energy production potential and cost estimates							
High ($EJ_{H2}\,yr^{-1}$)	299	25	82	162	43	2,509	3,121
Low ($EJ_{H2}\,yr^{-1}$)	58	24	3	41	8	154	288
High ($\mathrm{US\$\,kWh_{H2}^{-1}}$)	0.19	0.13	0.48	0.28	0.29	0.63	–
Low ($\mathrm{US\$\,kWh_{H2}^{-1}}$)	0.11	0.07	0.30	0.12	0.09	0.19	–
Global NE H_2 CO_2 removal potential and cost estimates							
High CO_2 ($Gt\,yr^{-1}$)	90	7	25	49	13	754	938
Low CO_2 ($Gt\,yr^{-1}$)	17	7	1	12	2	46	87
High ($\mathrm{US\$\ tCO_2^{-1}}$)	37	20	118	60	64	161	–
Low ($\mathrm{US\$\ tCO_2^{-1}}$)	14	3	66	17	9	37	–

The lower heating value of H_2 is used in the NE H_2 calculations. Low and high estimates are based on the minimum and mean or median electricity production potentials and electricity costs previously reported[27,28,34]. See text and Methods for rationale and NE H_2 value estimation procedures.

Table 2 | Stoichiometry of energy input and output, H_2 generation and CO_2 removal for the three NE H_2 schemes shown in Fig. 1, as well as for an assumed representative system of such methods

Method	Energy input (kJ_e / [mol CO_2 removed + X mols H_2 produced])	X (mol H_2 produced/ mol CO_2 removed)	Energy input (kJ_e / [mol H_2 produced + 1/X mol CO_2 removed])	Energy efficiency (EJ_{H2}/EJ_e)	$GtCO_2$ removed/EJ_e
Fig. 1a	200	0.5	400	0.61	0.22
Fig. 1b	300	0.5	600	0.41	0.15
Fig. 1c	309	0.7	464	0.53	0.14
Representative system	300	0.6	500	0.49	0.15

Data are from theory, modelling and experimentation as cited in Fig. 1 and further discussed in the Methods. The lower heating value of H_2, 242 $kJ\,mol^{-1}$, is used in these calculations.

economy' scenarios[30,32,33] that include greater integration of H_2 into (1) transportation fuels, (2) conventional grid electricity systems by providing energy storage (Supplementary Section 'Electricity sources and integration') and (3) conventional hydrocarbon fuel refining (Supplementary Section 'Integration into fossil energy'). We therefore believe that BECCS and NE H_2 can be complementary in addressing global fuel and electricity needs, greatly expanding global, negative-emissions energy generation potential.

Within biomass energy production, we note the much higher global energy capacity values for BECCS than for biomass-powered NE H_2 (Fig. 2). These higher BECCS values reflect the reporting[3] of global primary energy potential, 100–300 $EJ\,yr^{-1}$, rather than as electricity or H_2 as used in our analysis. However, the primary energy potentials for biomass energy reported by the IPCC[28], 21–116 $EJ\,yr^{-1}$, average lower than those reported in ref. [3].

Economics

Because commercial-scale NE H_2 systems have not been designed and demonstrated, estimating the cost of such systems is highly uncertain. Nevertheless, the following is an attempt at an initial economic assessment. Starting with the cost of input electricity, Table 1 lists the low and high costs of each renewable energy source (see Methods for derivation). We then divide the preceding low and high electricity cost values by the representative conversion efficiency of renewable electrical energy to NE H_2 (0.49, Table 2) to obtain the electricity cost ranges of NE H_2 in units of $\mathrm{US\$\,kWh_{H2}^{-1}}$ (Table 1). To this we add the other capital, operation and maintenance costs (see Methods) to obtain total NE H_2 cost ranges in $\mathrm{US\$\,kWh_{H2}^{-1}}$. The total undelivered energy production cost for NE H_2 thus varies from $\mathrm{US\$0.07\,kWh_{H2}^{-1}}$ using low-cost hydroelectricity to $\mathrm{US\$0.64\,kWh_{H2}^{-1}}$ using the highest-cost solar electricity (Table 1 and Fig. 3). Note that the within- and across-energy-source ranges of NE H_2 costs are only affected here by the range in the cost of renewable electricity ($\mathrm{US\$0.01–0.29\,kWh_e^{-1}}$, Table 1), which we believe is the dominant source of our NE H_2 cost estimation variability. A fuller consideration of system cost variation and uncertainties (when they become available) would expand these preliminary NE H_2 cost ranges.

For any given energy source the average cost of NE H_2 is about twice that of renewable electricity per kWh of energy produced, while the energy generation potential of NE H_2 is approximately half that of renewable electricity (Fig. 3). The most cost-effective sources of NE H_2 energy are hydro, geothermal, biomass and wind, with a total mean production potential of about 200 $EJ_{H2}\,yr^{-1}$ at costs ranging from US$0.07 to $\mathrm{US\$0.29\,kWh_{H2}^{-1}}$ (Fig. 3). These costs are generally below the cost range estimated for BECCS electricity (Fig. 3).

The marginal cost of CO_2 removal is estimated (see Methods) to range from $\mathrm{US\$3\,tCO_2^{-1}}$ (using lowest-cost hydroelectricity) to

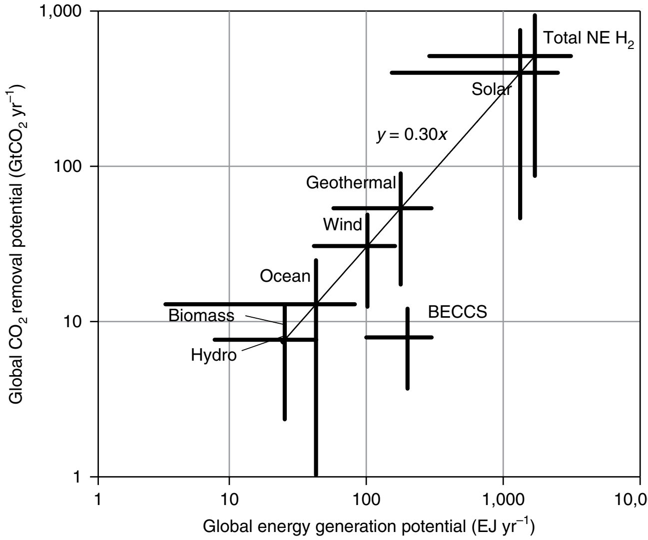

Fig. 2 | Global energy (H_2) generation potential versus global CO_2 removal potential for the NE H_2 process when powered by each of the electricity sources noted. Horizontal and vertical lines denote ranges of values derived from each electricity source as listed in Table 1. Previously reported[3] minimum and maximum parameter ranges for BECCS are also shown using primary energy units of EJ yr^{-1}.

US$161 tCO$_2^{-1}$ using the highest-cost solar electricity (Table 1). These costs are within or below the cost range of reducing fossil or biomass energy CO_2 emissions using CCS, US$50–150 tCO$_2^{-1}$ (ref. [34]). As in the case of NE H_2 energy production, the most cost-effective CO_2 removal and storage potential (US$3–60 tCO$_2^{-1}$) is obtained by the use of hydro, geothermal, biomass and wind electricity, with a summed removal capacity of about 100 Gt yr^{-1} (Fig. 4). Such costs are also equivalent to or significantly lower than those estimated for BECCS, while the summed CO_2 removal capacity of these four NE H_2 sources is about 8 times larger than BECCS (Fig. 4). Far greater removal capacities, though at higher average cost, are available using ocean and solar electricity (Fig. 4).

Additional issues and opportunities

The preceding sections describe a negative-emissions energy strategy with the potential to greatly expand the global resource beyond that previously estimated for BECCS, with the added benefits of (1) lessening or avoiding land use and land ecology impacts, (2) increasing the quantity of CO_2 removal per unit of energy generated, (3) avoiding the expensive production and risky storage of concentrated CO_2 inherent in CCS, and (4) achieving these benefits at estimated costs equivalent to or lower than BECCS. Carbon storage occurs in NE H_2 by converting CO_2 to dissolved alkaline bicarbonates and carbonates that, when added to the already very large reservoir of these compounds in the ocean, provide long-term carbon sequestration while helping counter ocean acidification[16,18,35].

Nevertheless, NE H_2 is not without its limitations, potential environmental impacts, and significant uncertainties that could greatly diminish its global potential, cost–benefit and desirability of use. These issues include (1) land use in energy and mineral harvesting, (2) water use for H_2 production and for carbon sequestration, (3) the availability and cost of low-emissions electricity, (4) the determination of optimum electrochemical cell materials, design, operation and economics, (5) the energy and CO_2-emission penalties of the preceding issues, (6) potential environmental impacts of such systems, and (7) the ability of H_2 to penetrate energy markets. See the Supplementary Information for a discussion of these topics.

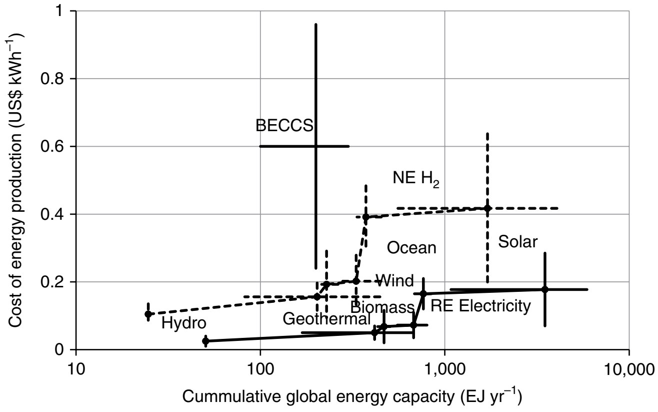

Fig. 3 | Supply-cost curves of cumulative potential global energy production versus cost of production (in ascending order of cost) for NE H_2 and for renewable electricity from the six renewable energy sources listed (Table 1). In the case of NE H_2, ranges of US$ kWh$_{H2}^{-1}$ and EJ$_{H2}$ yr^{-1} are depicted as dashed lines. Units of US$ kWh$_e^{-1}$ and EJ$_e$ yr^{-1} are used for renewable electricity (RE). The estimated[3] ranges are also shown for BECCS, where the reported[34] cost range of biomass electricity is increased by 80% to estimate a BECCS electricity cost range, consistent with the average cost increase of pulverized coal electricity when CCS is added[34] (see Methods).

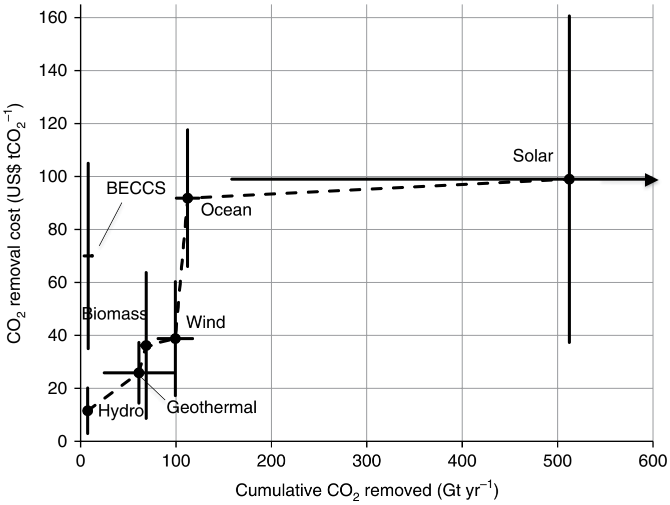

Fig. 4 | Supply-cost curve of cumulative CO_2 removal potential versus cost (in ascending order of cost) for NE H_2 employing the six electricity sources listed in Table 1. Horizontal and vertical lines denote the range of values for each electricity source (Table 1). Dashed lines used to connect mean values. Minimum and maximum ranges for BECCS are also shown, as previously reported[3].

This technology could also be integrated into conventional energy systems by providing a medium for energy storage or transport. For example, as noted above, NE H_2 could be used to store intermittent or off-peak grid electricity in the form of H_2, which could be converted (via fuel cells) back to electricity at high-value periods, while also imparting CO_2-emissions negativity to that storage. Additionally, nuclear-powered NE H_2 could offer a novel, negative-emissions, nuclear-to-fuels pathway. NE H_2 could also be used in conventional hydrocarbon refining to reduce, eliminate or reverse net CO_2 emissions from fuel use. Finally, any O_2 co-produced from NE H_2 could be used to oxyfire conventional, fossil-fuel combustion to produce greater combustion efficiency and higher-concentration waste CO_2 streams that would lower the cost of CCS. A fuller discussion of the preceding topics is provided in the Supplementary Information.

Conclusions

With the potential to utilize a broad range of renewable energy sources, NE H_2 significantly expands global, negative-emissions energy generation potential, assuming greatly increased H_2 and negative-emissions markets can be realized. It could also be useful in reducing the carbon footprint of conventional fuel and electricity production and of energy storage. It achieves these features by merging three separate technologies: renewable electricity, saline water electrolysis and enhanced mineral weathering. Further research is needed to determine the realizable capacity, economics and net environmental benefit of such systems. We also stress that the negative-emissions energy field is in its infancy and therefore the methods discussed here are unlikely to be the only ones ultimately worth considering (for example, refs [26,36–39]). CO_2 management strategies and research and development policies in the future therefore need to anticipate and encourage the emergence of additional approaches. This will maximize our chances of safely and cost-effectively increasing sustainable energy production while helping stabilize atmospheric CO_2, the climate and ocean acidification below the rapidly approaching critical thresholds.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available at https://doi.org/10.1038/s41558-018-0203-0.

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References

1. IPCC *Climate Change 2013: The Physical Science Basis* (eds Stocker, T. F. et al.) (Cambridge Univ. Press, 2013).
2. IPCC *Climate Change 2014: Mitigation of Climate Change* (eds Edenhofer, O. et al.) (Cambridge Univ. Press, 2014).
3. Smith, P. et al. Biophysical and economic limits to negative CO_2 emissions. *Nat. Clim. Change* **6**, 42–50 (2016).
4. Fuss, S. et al. Research priorities for negative emissions. *Environ. Res. Lett.* **11**, 115007 (2016).
5. Field, C. B. & Mach, K. J. Rightsizing carbon dioxide removal. *Science* **356**, 706–707 (2017).
6. Möllersten, K., Yan, J. & Moreira, J. R. Potential market niches for biomass energy with CO_2 capture and storage—opportunities for energy supply with negative CO_2 emissions. *Biomass Bioenergy* **25**, 273–285 (2003).
7. Boysen, L. R. et al. The limits to global-warming mitigation by terrestrial carbon removal. *Earth's Future* **5**, 463–474 (2017).
8. Fajardy, M. & Mac Dowell, N. Can BECCS deliver sustainable and resource efficient negative emissions? *Energy Environ. Sci.* **10**, 1389–1426 (2017).
9. Lenton, T. M. The global potential for carbon dioxide removal. *Issues Environ. Sci. Technol.* **38**, 52–79 (2014).
10. Hughes, A. D. et al. Does seaweed offer a solution for bioenergy with biological carbon capture and storage? *Greenh. Gas. Sci. Technol.* **2**, 402–407 (2007).
11. Little, M. G. & Jackson, R. B. Potential impacts of leakage from deep CO_2 geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.* **44**, 9225–9232 (2010).
12. Zoback, M. D. & Gorelick, S. M. Earthquake triggering and large-scale geologic storage of carbon dioxide. *Proc. Natl Acad. Sci. USA* **109**, 10164–10168 (2012).
13. Maddali, V., Tularam, G. A. & Glynn, P. Economic and time-sensitive issues surrounding CCS: a policy analysis. *Environ. Sci. Technol.* **49**, 8959–8968 (2015).
14. Gasser, T., Guivarch, G., Tachiiri, K., Jones, C. D. & Ciais, P. Negative emissions physically needed to keep global warming below 2 °C. *Nat. Commun.* **6**, 8958 (2015).
15. Hansen, J. et al. Young people's burden: requirement of negative CO_2 emissions. *Earth Syst. Dynam.* **8**, 577–616 (2017).
16. House, K. Z., House, C. H., Schrag, D. P. & Aziz, M. J. Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. *Environ. Sci. Technol.* **41**, 8464–8470 (2007).
17. Rau, G. H. Electrochemical splitting of calcium carbonate to increase solution alkalinity: implications for mitigation of carbon dioxide and ocean acidity. *Environ. Sci. Technol.* **42**, 8935–8940 (2008).
18. Rau, G. H. et al. Direct electrolytic dissolution of silicate minerals for air CO_2 mitigation and carbon-negative H_2 production. *Proc. Natl Acad. Sci. USA* **110**, 10095–10100 (2013).
19. Lu, L., Huang, Z., Rau, G. H. & Ren, Z. J. Microbial electrolytic carbon capture for carbon negative and energy positive wastewater treatment. *Environ. Sci. Technol.* **49**, 8193–8201 (2015).
20. Willauer, H. D., DiMascio, F., Hardy, D. R. & Williams, F. W. Development of an electrolytic cation exchange module for the simultaneous extraction of carbon dioxide and hydrogen gas from natural seawater. *Energy Fuels* **31**, 1723–1730 (2017).
21. Rau, G. H. & Caldeira, K. Enhanced carbonate dissolution: a means of sequestering waste CO_2 as ocean bicarbonate. *Energy Convers. Manag.* **40**, 1803–1813 (1999).
22. Rau, G. H. CO_2 mitigation via capture and chemical conversion in seawater. *Environ. Sci. Technol.* **45**, 1088–1092 (2011).
23. de Lannoy, C.-F. et al. Indirect ocean capture of atmospheric CO_2: Part I. Prototype of a negative emissions technology. *Int. J. Greenh. Gas Control* **70**, 254–261 (2018).
24. Licht, S. Efficient solar-driven synthesis, carbon capture, and desalinization, STEP: solar thermal electrochemical production of fuels, metals, bleach. *Adv. Mater.* **23**, 5592–5612 (2011).
25. Ren, J. W., Li, F. F., Lau, J., Gonzalez-Urbina, L. & Licht, S. One-pot synthesis of carbon nanofibers from CO_2. *Nano Lett.* **15**, 6142–6148 (2015).
26. Li, F. F. et al. Solar fuels: a one-pot synthesis of hydrogen and carbon fuels from water and carbon dioxide. *Adv. Energy Mater.* **5**, 1401791 (2015).
27. IPCC *Special Report on Renewable Energy Sources and Climate Change Mitigation* (eds Edenhofer, O. et al.) (Cambridge Univ. Press, 2012).
28. Bruckner, T. et al. in *Climate Change 2014: Mitigation of Climate Change* (eds Edenhofer, O. et al.) Ch. 7 (IPCC, Cambridge Univ. Press, 2014).
29. *Key World Energy Statistics* (International Energy Agency, 2017).
30. Study Task Force of the Hydrogen Council *Hydrogen—Scaling up a Sustainable Pathway for the Global Energy Transition* (The Hydrogen Council, 2017).
31. Le Quéré, C. et al. Global Carbon Budget 2017. *Earth Syst. Sci. Data Discuss.* https://doi.org/10.5194/essd-2017-123 (2017).
32. National Research Council *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs* (National Academies, 2004).
33. McDowall, W. & Eames, M. Forecasts, scenarios, visions, backcasts and roadmaps to the hydrogen economy: A review of the hydrogen futures literature. *Energy Policy* **34**, 1236–1250 (2006).
34. IPCC *Climate Change 2014: Mitigation of Climate Change* (eds Edenhofer, O. et al.) Annex III (Cambridge Univ. Press, 2014).
35. Renforth, P. & Henderson, G. Assessing ocean alkalinity for carbon sequestration. *Rev. Geophys.* **55**, 636–674 (2017).
36. Hanak, D. P., Jenkins, B. G., Kruger, T. & Manovic, V. High-efficiency negative-carbon emission power generation from integrated solid-oxide fuel cell and calciner. *Appl. Energy* **205**, 1189–1201 (2017).
37. Nikulshina, V., Hirsch, D., Mazzotti, M. & Steinfeld, A. CO_2 capture from air and co-production of H_2 via the $Ca(OH)_2$-$CaCO_3$ cycle using concentrated solar power—thermodynamic analysis. *Energy* **31**, 1715–1725 (2006).
38. Licht, S. et al. Carbon nanotubes produced from ambient carbon dioxide for environmentally sustainable lithium-ion and sodium-ion battery anodes. *ACS Cent. Sci.* **2**, 162–168 (2016).
39. Rau, G. H. & Baird, J. R. Negative-CO_2-emissions ocean thermal energy conversion. *Renew. Sustain. Energy Rev.* (in the press).

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Author contributions

G.H.R. conceived of and led the project, analysed data and wrote the paper. H.D.W and Z.J.R provided data and helped write the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Methods

Global H_2 generation and CO_2 removal potentials. Because NE H_2 must be powered by non-fossil electricity to achieve maximum net CO_2-emissions negativity, we start our estimation process by using previously reported[27,28] ranges for technical, potential electricity production for six categories of renewable energy sources (Table 1). In the case of biomass and solar energy, however, primary energy rather than electrical energy was originally reported. To convert these to electrical energy, conversion efficiencies of 32% and 20%, respectively, are assumed[28]. For the purposes of this Article we use a low and high source electricity capacity range as defined by the minimum and median or mean values rather then the originally reported minimum and maximum values. This reflects more conservative global renewable electricity production ranges that are probably more representative of the electrical energy resources theoretically available for the application we envision.

The resulting potential electricity supply ranges (rows 1 and 2, Table 1), are then converted to NE H_2 energy production ranges using a representative energy conversion efficiency of 0.49 (range 0.41–0.61, Table 2), and using the lower heating value (LHV) of H_2, 242 kJ mol^{-1}. This reference case is derived from the three separate NE H_2 examples shown in Fig. 1 and listed in Table 2. In the example in ref. [20] (Fig. 1c), extraction of a concentrated CO_2 gas stream from acidified seawater was originally reported, with the intent of synthesizing hydrocarbon fuel from this and from the co-produced H_2. Instead, to convert this to an NE H_2 production system, we propose reacting the $CO_2(aq)$ (carbonic acid) concentrated in seawater (before degassing) with $CaCO_3(s)$ (for example, limestone) to spontaneously convert the dissolved $CO_2(aq)$ to $Ca(HCO_3)_2(aq)$ (Fig. 1c). However, this reaction is at best only about 80% efficient in consuming excess CO_2 (ref. [22]), and we conservatively assume 50% efficiency for the present calculations. This CO_2 removal is in addition to that effected by the release of the system's produced dissolved mineral hydroxide into seawater and its subsequent consumption of CO_2 (Fig. 1c). Dividing the global electricity ranges (rows 1 and 2, Table 1) by 0.49 thus yields the NE H_2 energy ranges and totals in $EJ_{H2}\,yr^{-1}$ (rows 5 and 6, Table 1).

In comparing NE H_2 to BECCS energy production potential, we assume that the energy produced in the form of H_2 and the primary or electrical energy produced by BECCS can be compared using common units of EJ yr^{-1}. We also assume that either form of energy production qualifies as 'negative-emissions energy' and can be considered in strategies where the form of the negative-emissions energy required is unspecified (for example, IPCC scenarios). Obviously, the quantity of NE H_2 and BECCS ultimately used (below technical maximums) will be dictated by policy and market forces.

The global CO_2 removal potentials for NE H_2 (rows 9 and 10, Table 1) are estimated by dividing the potential electricity generation ranges (rows 1 and 2, Table 1) by the representative 0.15 $GtCO_2$ removed per EJ_e (Table 2).

Estimation of NE H_2 economics. In estimating the cost ranges for NE H_2, we start with the cost of input electricity from a given source. Table 1 (rows 3 and 4) lists the low and high costs of each renewable energy source as reported by IPCC[27]. However, here we equate the high cost values to the reported[27] mean or median US$ kWh_e^{-1} and the low cost estimates to the reported[27] minimum US$ kWh_e^{-1} values. We use these values rather than the minimum and maximum values because cost values above the mean are likely to be more representative of the minimum to mean or median input electricity generation potentials considered in our analysis. That is, costs above the mean cost of a given renewable electricity source will primarily be relevant only when global energy potentials are fully exploited, which we elect to avoid in our analysis. Not using present maximum electricity cost values is also justified because electricity production cost will probably be lower in the future due to technological advances that reduce capital costs and increase primary energy to electricity conversion efficiencies, the recent declines in wind and solar electricity production costs (post-dating the values used in this study) being prime examples of this[40,41].

From the preceding US$ kWh_e^{-1} values we then calculate the electricity cost for NE H_2 energy production as US$ kWh_{H2}^{-1} = (US$ kWh_e^{-1})/0.49, given the representative energy conversion efficiency listed in Table 2. Other capital, operation and maintenance costs must then be added to this energy cost, which is estimated to total an additional fixed cost of US$0.05 kWh_{H2}^{-1}. This is derived from a previous assessment[18] where (1) electrolyser cost is equivalent to US$14 tCO_2^{-1} removed, (2) ground and delivered mineral costs are US$24 tCO_2^{-1} removed (Supplementary Section 'Minerals'), (3) water pumping costs are US$2 tCO_2^{-1} removed, (4) additional operation and maintenance costs are US$0.42 tCO_2^{-1} removed, and (5) H_2 pressurization costs are excluded. The total is thus US$14 + US$24 + US$2 + US$0.42 = US$40.42 tCO_2^{-1} removed. Given that 1.67 mol CO_2 are removed per mol of H_2 produced (Table 2), the lower heating value of H_2 is 242 kJ mol^{-1} (0.067 kWh mol^{-1}), and that 1 tCO_2 = 22,727 mol CO_2, the H_2 production cost equivalent (excluding electricity) is US$0.044 kWh_{H2}^{-1}, which, to be cautious, we round up to US$0.05 kWh_{H2}^{-1}. This is then added to the electricity-only H_2 production cost ranges calculated above, to arrive at a total cost range in units of US$ kWh_{H2}^{-1} for each of the renewable energy sectors listed (rows 7 and 8, Table 1).

To determine a representative US$ kWh_e^{-1} cost range for electricity produced by BECCS, we took the reported cost range of biomass electricity[34] and then increased this by 80% to estimate a BECCS electricity cost range, paralleling the average percentage increase in the cost of pulverized coal electricity when CCS is added[34]. This BECCS US$ kWh_e^{-1} range is shown in Fig. 3.

The marginal cost of CO_2 removal is calculated as:

$$\mathrm{US\$/tCO_2} = (a - B) \times C \times D$$

where a is the low or high NE H_2 production cost (US$ kWh_{H2}^{-1}) (rows 7 and 8, Table 1), B is the value of the undistributed and unpressurized H_2 produced, here assumed to be US$2 per kg H_2 or US$0.06 $kWh_{H2(LHV)}^{-1}$, equivalent to the production cost of conventional, steam-reformed methane-generated, unpressurized H_2 (ref. [42]), and C is the fraction of the net H_2 cost expenditure that is attributable to CO_2 removal (0.30). This fraction is derived by differencing the average energy efficiency of alkaline electrolytic H_2 production (0.70; total range 54–85%, ref. [43]), and the representative energy efficiency of NE H_2 (0.49, Table 2), which is a 30% loss in efficiency, or a 30% increase in energy use to achieve C negativity. It is then assumed that the remaining, marginal non-energy cost of NE H_2 CO_2 removal composes the same fraction, such that total CO_2 removal cost (US$ kWh_{H2}^{-1}) = 0.30 × total NE H_2 cost. Finally, D = 924 kWh_{H2} tCO_2^{-1} as dictated by the 0.49 EJ_{H2} per 0.15 $GtCO_2$ removed in the reference NE H_2 case (Table 2) so that US$ kWh_{H2}^{-1} is converted to US$ tCO_2^{-1}. Note that the preceding assumes that the hydroxide produced by the system can be diluted and added directly to the ocean to effect ocean/air CO_2 removal without the need for costly, engineered, air contacting systems[16,18].

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

References

40. Fu, R. et al. *U.S. Solar Photovoltaic System Cost Benchmark: Q1 2017* Technical Report NREL/TP-6A20-68925 (US National Renewable Energy Laboratory, 2017).
41. Mone, C. et al. *2015 Cost of Wind Energy Review* Technical Report NREL/TP-6A20-66861 (US National Renewable Energy Laboratory, 2017).
42. *Hydrogen Production: Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan—Planned Program Activities for 2011–2020* (Energy Efficiency and Renewable Energy Program, US Department of Energy, 2015).
43. Gahleitner, G. Hydrogen from renewable electricity: an international review of power-to-gas pilot plants for stationary applications. *Int. J. Hydrog. Energy* **38**, 2039–2061 (2013).