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**Perspective** 

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# Scaling and heating will drive low-temperature CO<sub>2</sub> electrolysers to operate at higher temperatures

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Henri M. Pelzer M., Nikita Kolobov, David A. Vermaas M. Thomas Burdyny M.

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Low-temperature carbon dioxide electrolysis (CO<sub>2</sub>E) provides a one-step means of converting CO<sub>2</sub> into carbon-based fuels using electrical inputs at temperatures below 100 °C. Over the past decade, an abundance of work has been carried out at ambient temperature, and high CO<sub>2</sub>E rates and product selectivities have been achieved. With scaling of CO<sub>2</sub>E technologies underway, greater discourse surrounding heat management and the viable operating temperatures of larger systems is important. In this Perspective we argue that, owing to the energy inefficiency of electrolysers, heat generation in CO<sub>2</sub>E stacks will favour operating temperatures of between 40 and 70 °C, far from the ambient temperatures used so far. Such elevated temperatures put further pressure on catalyst and membrane stability and on the stack design. On the other hand, elevated temperatures could alleviate challenges in salt precipitation, water management and high cell voltages, aiding the technology. We reflect on these aspects and discuss the opportunities for waste heat valorization to increase the economic feasibility of the process.

The heavy decarbonization of society is essential for maintaining and improving the standard of living of humankind. One key sector for decarbonization is the chemical industry, which relies heavily on fossil fuel resources such as oil and natural gas<sup>1</sup>. Many chemicals are carbon-based, making carbon neutrality particularly challenging. One potential low-carbon pathway for producing base chemicals is carbon dioxide electrolysis (CO<sub>2</sub>E), utilizing green energy and captured CO<sub>2</sub>. CO<sub>2</sub>E is capable of selectively producing chemical building blocks such as carbon monoxide (CO) and ethylene2.

Low-temperature CO<sub>2</sub>E is currently well-established on the laboratory scale, with larger cell and stack demonstrations becoming more frequent<sup>3</sup>. The most efficient and scalable configurations utilize a CO<sub>2</sub> gas-fed membrane electrode assembly (MEA) 'zero gap' cell. Whereas bipolar membranes hold promise for providing a stable KOH anolyte, enabling the use of earth-abundant anode materials, anion exchange membranes (AEMs) are still commonly applied<sup>4</sup>. At elevated current densities, reported state-of-the-art energy efficiencies range from 30 to 60% (refs. 5,6), leading to cell voltages of between 2.3 and 4.7 V (ref. 7). If water acts as a proton donor the energy efficiency is thermodynamically limited to a maximum of 62% (ref. 6). Thus, approximately 40-70% of the input electricity is dissipated as heat, which is substantially higher than the approximately 35% value of proton exchange membrane (PEM) water electrolysers with a similar architecture<sup>8</sup>. As laboratory-scale CO<sub>2</sub>E devices are on the order of 10 W, the ~5 W of heat released goes primarily unnoticed or is reported to dissipate from the electrolyser, tubing and electrolyte. Looking to future CO<sub>2</sub>E systems of 0.1-1 MW, however, the amount of heat to be dissipated becomes substantial and needs to be accounted for in the plant design and system integration. An additional consequence of heat generation is temperature gradients within the CO<sub>2</sub>E stack.

Within the CO<sub>2</sub>E research field, experiments have been conducted predominantly at ambient temperature (20-25 °C). Such accessible operating conditions have enabled researchers with different research specializations and laboratory capabilities to quickly enter the field and perform research at the 1–10 W scale. The testing of <10 W systems at higher temperatures (>40 °C) has been comparatively limited 9-11,

Department of Chemical Engineering, Delft University of Technology, Delft, Netherlands. Me-mail: h.p.pelzer@tudelft.nl; t.e.burdyny@tudelft.nl

although these temperatures are near uniform in reports that use larger cells or stacks  $^{9,12}$ . Recent literature reports demonstrating CO $_2$ E stacks on the kilowatt scale  $^{13,14}$ , for example, have shown that the inefficiency of electrolysers causes cell and anolyte temperatures to rise rapidly to temperatures of >50 °C in the absence of active heat-removal measures, thus leading to higher operation temperatures  $^{12}$ . This poses a dilemma: either operate at 20–25 °C, leveraging existing knowledge but assuming that future CO $_2$  electrolyser stacks will be heavily cooled, or embrace the challenges and opportunities that come with operation at elevated temperature. Such a decision impacts not only system integration and overall energetics but also the multitude of temperature-dependent parameters that influence the CO $_2$ E performance metrics.

In this Perspective we argue that unavoidable heat generation will force even modestly sized  $CO_2E$  stacks to operate at temperatures between 40 and 70 °C. Greater research activities must then shift towards higher-temperature testing, not only to pre-emptively overcome new unexpected challenges but also to benefit from the operating regime. Although looking at electrolyser heating may appear minor at first, we show that it induces non-linear changes in  $CO_2$  and salt solubility, vapour pressure, electrode kinetics, conductivity, water transport and catalyst stability. We close with a discussion on the potential efficiency upsides of heat recuperation on the process level.

#### Heat sources and sinks in CO<sub>2</sub> electrolysers

In state-of-the-art zero-gap MEA cells, gaseous humidified  $CO_2$  is supplied on the cathode side. The  $CO_2$  then diffuses through a porous layer to a liquid-immersed catalyst layer where  $CO_2$  reduction takes place. The cathode and anode are separated by an AEM<sup>15-17</sup>, with a liquid electrolyte positioned next to the oxygen-evolving anode. The entire thickness of the above cell components normally is <3 mm. To form a stacked electrolyser, cells are placed adjacent to one another in either a unipolar or a bipolar design (see Fig. 1a)<sup>3</sup>. Keeping in mind industrially relevant current density (j) values of >200 mA cm<sup>-2</sup>, we can compare the sources and sinks of heat within a  $CO_2$ E stack<sup>2,17,18</sup>.

A basic heat balance of a CO<sub>2</sub>E stack is shown in Fig. 1a and displayed in equation (1):

$$0 = \dot{Q}_{gas} + \dot{Q}_{lig} + \dot{Q}_{surf} - \dot{Q}_{n+\Omega}.$$
 (1)

The relevant heat sources are characterized by  $\dot{Q}_{\eta+\Omega}$ , that is, the heat released by the excess overpotential to drive the electrochemical reactions and to overcome ohmic resistances. The entropic effects of mixing gases are ignored. The parameter  $\dot{Q}_{\eta+\Omega}$  is proportional to the potential  $U_{\eta+\Omega}$ , which is defined as the difference between the applied cell/stack potential ( $U_{\text{cell}}$ ) and the thermoneutral potential of the reaction ( $U_{\text{th}}$ ). The parameter  $U_{\eta+\Omega}$  is then multiplied with the total current (i) passed in the electrolyser to calculate  $\dot{Q}_{\eta+\Omega}$  (equation (2)):

$$\dot{Q}_{n+\Omega} = U_{n+\Omega} i = (U_{\text{cell}} - U_{\text{th}}) i. \tag{2}$$

The excess overpotential that results in heat generation occurs across the cell and can be split into several distinct components. These include reaction overpotentials of the cathode and anode reactions ( $\eta_{\text{cath}}$  and  $\eta_{\text{an}}$ , respectively), the voltage drop over the AEM ( $U_{\text{AEM}}$ ), and the voltage drop over the contact resistance at the membrane-cathode interface ( $U_{\text{C,cath}}$ ) or the membrane-anode interface ( $U_{\text{C,an}}$ ) (Fig. 1b)<sup>19,20</sup>. Part of the required overpotentials drives the electrochemical reactions to split water, which acts as a proton donor for  $\text{CO}_2$  reduction. Heat then dissipates when the by-product hydroxide from water splitting reacts with  $\text{CO}_2$  to form carbonate at the cathode (see Fig. 1c). Carbonate is then itself neutralized by protons near the anode after crossing the AEM. Whereas heat is released during both of the neutralization reactions, their heating effect is effectively included within the reaction overpotentials in equation (2). On a last note, experimental data have suggested that the contact resistance values between the

components are an especially important contributor to the ohmic resistance, accounting for 80% of the accumulated ohmic drop over the membrane and interfaces, stressing the importance of interface engineering<sup>21</sup>. Despite the relevance of  $\eta_{\text{cath}}$  and  $\eta_{\text{an}}$  for lower current densities, the kinetic part of the overpotential scales logarithmically with the applied current, decreasing its impact at higher current densities<sup>19,20</sup>.

To achieve steady-state operation, the heat sources must be countered by heat sinks (equation (1)). In a standard  $CO_2E$  stack, the available sinks are advection via the gas stream  $\dot{Q}_{\rm gas}$  on the cathode side and the liquid anolyte stream  $\dot{Q}_{\rm liq}$  on the anode side. In addition, heat can leave the system via the stack's outer surface  $\dot{Q}_{\rm surf}$  (Fig. 1a). All of those heat sinks require a temperature gradient to transport heat:  $\dot{Q}_{\rm surf}$  is transported over the gradient between the stack temperature and ambient temperature, whereas  $\dot{Q}_{\rm gas}$  and  $\dot{Q}_{\rm liq}$  can be defined via the respective inlet and outlet temperatures of the gas and liquid streams. A qualitative assessment of the resistance ( $R_{\rm surf}$ ) and capacity ( $C_{\rm th,gas}$  and  $C_{\rm th,liq}$ ) values in equations (3)–(5) can then be carried out to show the contribution of each sink using an equivalent thermal resistance and thermal capacity comparison, assuming similar magnitudes of the temperature gradients<sup>22</sup>.

$$R_{\rm surf} = \frac{1}{h_{\rm eff}A} \tag{3}$$

$$C_{\rm th,gas} = \dot{m}_{\rm gas} c_{p,\rm gas} \tag{4}$$

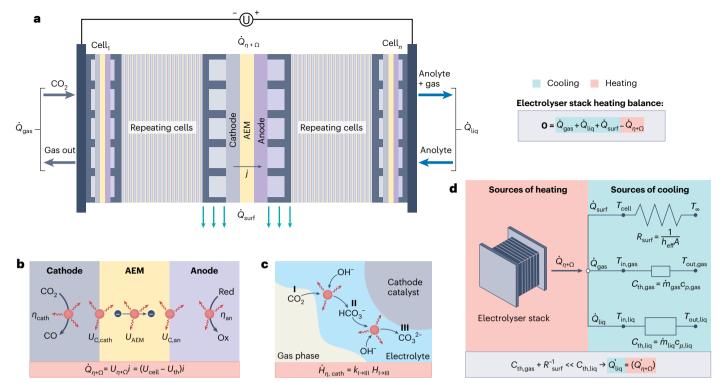
$$C_{\rm th,liq} = \dot{m}_{\rm liq} c_{p,\rm liq} \tag{5}$$

Whereas a detailed heat- and mass-transport analysis is beyond the scope of this work, an order-of-magnitude analysis of equations (3)-(5) indicates that the analyte will be predominantly responsible for heat removal from an electrolyser stack (Fig. 1d). Owing to the around fourfold larger specific heat capacity  $(c_n)$  and the about 500-fold larger density ( $\rho$ ) of liquid water compared with CO<sub>2</sub> gas, we can expect the liquid analyte stream to remove several orders of magnitude more heat than the humidified gas stream. Similarly, surface cooling (equation (3)) can be assumed to be negligible given the poor heat transfer coefficient ( $h_{\rm eff}$ ) of, for example, natural convection and the low external surface area A of an electrolyser  $^{22}$ . For stacks in particular, the external surface area increases minimally when the number of cells is increased, whereas heat generation scales in direct proportion to the total cell area. In other words,  $\dot{Q}_{\rm lig} \gg (\dot{Q}_{\rm gas} + \dot{Q}_{\rm surf})$ . The importance of the anolyte stream for heat removal has been demonstrated further in recent literature reports<sup>13,14</sup>. Understanding that the analyte is responsible for most heat removal enables us to predict the eventual operating temperature of a larger-scale CO<sub>2</sub> electrolyser.

### Temperature operation range and spatial distribution

The anolyte is typically recirculated over the electrolyser (Fig. 2a). Thus, while heat can be removed from the electrolyser with each pass, it will accumulate within the anolyte circuit. Without a balanced heat removal from the whole system, temperatures will quickly approach the thermal stability limits of most AEMs at  $70-80\,^{\circ}\text{C}$  (refs. 21,23) and the boiling point of the anolyte at around  $100\,^{\circ}\text{C}$  (see Fig. 2b). Such heat accumulation has been illustrated in a  $CO_2E$  stack that uses cooling channels between the cells to mitigate the temperature increase<sup>14</sup>.

The two cooling choices that exist are either to cool down the  $\rm CO_2E$  stack directly or remove heat from the anolyte circuit. Direct cooling of a large stack requires the addition of cooling channels within each unit cell. The addition of cooling channels then complicates the stack assemblies, which already require a high tolerance to prevent sealing



**Fig. 1**| **Heat balance analysis for CO\_2E stack. a**, Heat sinks and sources within a state-of-the-art CO $_2$ E stack comprising of the heat transfer rates for the liquid stream  $\dot{Q}_{\rm liq}$ , the gas stream  $\dot{Q}_{\rm gas}$ , surface cooling  $\dot{Q}_{\rm surf}$  and cell overpotentials and ohmic losses  $\dot{Q}_{\eta+\Omega}$ . **b**, Location and visualization of heat generation associated with  $\dot{Q}_{\eta+\Omega}$  expressed via the overpotentials and ohmic losses potential  $U_{\eta+\Omega}$  and the current i.  $U_{\eta+\Omega}$  can be expressed as the difference between cell voltage  $U_{\rm cell}$  and thermoneutral potential  $U_{\rm th}$ . Red, reduction; Ox, oxidation. **c**, As a consequence of acid–base neutralization, the resulting reaction heat transfer rate at the

cathode  $\dot{H}_{\eta,{\rm cath}}$  is given by the reaction rate  $k_{\rm I\to III}$  and reaction enthalpy  $H_{\rm I\to III}$ .  ${\bf d}$ , Balance of heat sources and sinks showing the thermal equivalent circuit model of the respective capacities of the heat sinks via advection of the gas stream ( $C_{\rm th,gas}$ ) and the anolyte stream ( $C_{\rm th,liq}$ ), and the thermal resistance of surface cooling  $R_{\rm surf}$ . Temperature differences are given by the streams' inlet and outlet temperatures  $T_{\rm in/out,ir}$ , the cell/stack temperature  $T_{\rm cell}$  and the ambient temperature  $T_{\rm cell}$ . The mass flow rates of the gas and liquid stream are given by  $\dot{m}_{\rm gas}$  and  $\dot{m}_{\rm lig}$ , respectively.

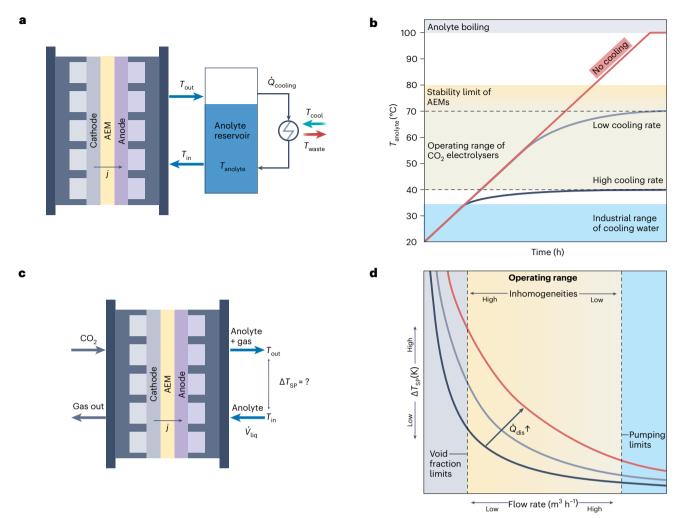
and puncturing issues. However, if issue-free assembly is ensured, direct cooling poses an additional heat sink close to the heating source. Some PEM water electrolysers utilize internal stack cooling, which can act as a design basis for  $CO_2E$  stacks. The alternative method of stack cooling, namely removing heat from a liquid circuit, is well understood through traditional heat exchangers and thus poses a viable alternative<sup>3</sup>.

Both options above require the temperature of the cooling fluid to be lower than the electrolyser temperature, which sets a lower limit for a stack's operating temperature. For heat exchangers to have a high effectiveness, the temperature difference between the anolyte circuit and the cooling fluid should be at least 10 K, with higher temperature differences more favoured economically<sup>22</sup>. Thus, to operate electrolysers at room temperature, chilled water (5-15 °C) would be required as a cooling source<sup>24,25</sup>, with substantial energy costs associated with continuously cooling the source water. An alternative is to use industrial cooling water, as shown in Fig. 2b, which is more commonly available in industrial plants for a temperature range of 27–35 °C (refs. 24,25). With this range in mind, a minimum achievable steady-state  $T_{\text{anolyte}}$  would be ~40 °C using a high exchange surface area. Using lower cooling rates and thus smaller heat exchanger devices or less industrial cooling water would push the steady-state  $T_{\text{anolyte}}$  higher. In addition, higher operation temperatures can unlock more economic heat exchangers, for example, air/liquid heat exchangers. The upper operation limit is given by the AEM stability limit, which is typically at 70–80 °C. A membrane with increased temperature stability could extend the upper temperature limit, increasing the heat exchanger economics while providing a wider range for the optimum operation temperature. However, we argue that the operating range of  $CO_2$  electrolysers will fall within the range of 40–70  $^{\circ}\text{C}.$ 

A parallel but important discussion is the desired temperature gradient within the electrolyser itself. This aspect is illustrated in Fig. 2c where the difference between  $T_{\rm in}$  and  $T_{\rm out}$  is highlighted as  $\Delta T_{\rm SP}$ , the single-pass spatial temperature gradient. As the anolyte is responsible for most heat removal, the temperature difference and gradient within a stack can be adjusted via the anolyte flow rate. However, flow rates cannot be chosen freely.

The upper limit of the anolyte flow is limited by pressure drops through the system and hence the pumping cost. Simulations of different flow fields in a PEM electrolyser show that the pressure drop can increase by up to 7 bar (ref. 26). At higher pressure drops, the pressure distribution also varies more severely, leading to a spatial dependence of the differential pressure, which affects the local reaction environments <sup>27</sup>. In addition, the flow field needs to fulfil the role of a current collector <sup>26</sup>. The lower limit of the fluid flow is linked to the removal of  $CO_2$  and  $O_2$  gas bubbles evolving in the anolyte stream: too low a flow rate leads to gas build-up and an inhomogeneous water supply at the anode <sup>28</sup>. In the case where the maximum applicable flow rate does not yield sufficient cooling, the need for additional direct cooling within the stack becomes inevitable.

A separate aspect of a high  $\Delta T_{\rm SP}$  is the introduction of spatial inhomogeneities to the stack, which have multiple disadvantages. Higher spatial temperature gradients will, for example, put variable mechanical stresses on different components, shortening the lifetime of the system<sup>29</sup>. This local difference in ageing, together with a local dependency of current density and selectivity due to the temperature differences,



 $\label{eq:cooling} \textbf{Fig. 2} \ | \ \textbf{Operable temperature range and single-pass spatial temperature} \\ \textbf{gradient. a}, \ \textbf{Operable temperature for CO}_2 \textbf{E} \ \text{stacks operating under a current} \\ \textbf{density} \ (j) \ \text{with applied cooling at the anolyte circuit using a cooling heat duty} \\ \dot{Q}_{\text{cooling}}, \ \textbf{cooling agent temperature} \ T_{\text{cool}} \ \text{and return temperature} \ T_{\text{waste}}, \\ \textbf{b}, \ \textbf{Development of the anolyte temperature} \ T_{\text{anolyte}} \ \text{over operation time}. \\ \textbf{The maximum anolyte temperature is imposed by the AEM stability}. \\ \textbf{The electrolyte temperature} \ \text{at the electrolyser inlet} \ (T_{\text{in}}) \ \text{is equal to} \ T_{\text{anolyte}} \ \text{and is} \\ \textbf{lower than the outlet temperature} \ \text{of the electrolyser} \ (T_{\text{out}}). \ \textbf{The minimum} \\ \end{aligned}$ 

temperature is given by the temperature level  $T_{\rm cool}$  and the applicable cooling rate of the heat exchanger transporting the heat duty.  ${\bf c}$ , Analysis of the single-pass spatial temperature gradient  $\Delta T_{\rm SP}$ , which influences the level of inhomogeneities to the  ${\rm CO_2}$  stack.  ${\bf d}$ , Development of  $\Delta T_{\rm SP}$  depends on the anolyte flow rate  $\dot{P}_{\rm liq}$  as well as the overall dissipating heat transfer rate  $\dot{Q}_{\rm dis}$  from the  ${\rm CO_2E}$  stack and is limited by the pumping cost and operable void fraction. The cooling rate can be further enhanced by additional direct cooling.

increases complexity of the stack. It has been demonstrated that water management in  $\mathrm{CO_2E}$  MEA cells is already highly complex in homogeneous environments, and spatial temperature variations could exacerbate drying out, condensation or flooding events<sup>30–32</sup>.

## Temperature effects on the performance of CO<sub>2</sub> electrolysers

The cell performance for  $CO_2E$  is influenced by a multitude of phenomena that range from the ångström to the millimetre scale. Table 1 presents an overview of the most relevant phenomena and properties for  $CO_2E$  in an MEA cell and thus also an industry-scale  $CO_2E$  stack, both at ambient temperature and in the proposed temperature range of 40–70 °C.

As an output metric, the applied cell voltage is one of the most important figures of merit, as the majority of the  $\mathrm{CO}_2\mathrm{E}$  stack costs are governed by the electric power input<sup>33</sup>. Literature reports indicate that a higher temperature is kinetically favourable, and the electrolyte and AEM conductivity will be increased, both decreasing the electric power needed at higher temperatures <sup>9,10</sup>. The benefits of temperature on the cell voltage are illustrated in ref. 13.

On the other hand, there is an almost 2.5-fold decrease in CO<sub>2</sub> solubility between 25 and 70 °C (ref. 34), which could challenge the dissolution of gaseous CO<sub>2</sub> and it reaching the entirety of the catalyst layer<sup>35</sup>. Elevated temperatures could then proportionally lower the maximum current density values towards carbon-based products due to an insufficient CO<sub>2</sub> supply. This would manifest as a lower Faradaic efficiency (FE), a parameter that describes the portion of electrons contributing to a certain product. Selectivity and the FE are considered to be similar in CO<sub>2</sub>E. As both higher current densities and an FE of >80% towards carbon-based products is desired to ensure economic feasibility<sup>29</sup>, it is important that lower solubilities are not inhibiting the performance. Fortunately, existing reports indicate that highly selective and high-rate CO production on silver can proceed at higher temperatures7. In addition, any larger electrolyser stack will undoubtedly require at least mildly elevated pressures to offset pressure drops in the gas and liquid channels. The counter effects of pressure on CO<sub>2</sub> solubility are shown in Fig. 3b.

A secondary effect of temperature is its influence on adsorption-desorption and the reaction kinetics, which can impact the product selectivity. This is particularly the case for copper-based catalysts,

Table 1 | Non-exhaustive list of CO₂E stack system properties at various temperatures

	Temperature (°C)			D-f
Property	25	40	70	— Ref.
Heat sinks				
		Heat capacity (k.	Imol <sup>-1</sup> K <sup>-1</sup> )	
C <sub>p,H2</sub> O	4.178	4.179	4.192	22
C <sub>p,CO2</sub>	0.849	0.858	0.894	22
		Density (kg	m <sup>-3</sup> )	
O <sub>H2</sub> O	998.0	991.1	977.5	22
$o_{CO_2}$	1.785	1.587	1.546	22
Salt formation				
	Salt solubility (mol l <sup>-1</sup> )			
CsHCO <sub>3</sub>	12.91ª	16.11ª	23.93ª	44
Cs₂CO₃	8.11ª	8.77ª	9.59ª	44
KHCO <sub>3</sub>	3.63	4.53	6.73	45
<₂CO₃	8.17	8.47	9.66	45
Water manage	ment/membra	ne <sup>b</sup>		
		Conductivity (n	nScm <sup>-1</sup> )	
σ <sub>OH</sub> -	72.4	90.8	127.7	46
J <sub>HCO3-</sub>	26.3	38.2	60.1	46
	G	Bas loading (g <sub>H2</sub> 0	kg <sub>CO2</sub> -1)	
V <sub>sat,H2</sub> O,CO <sub>2</sub>	12.29	30.84	193.96	47
	CO <sub>2</sub> so	lubility (mmol <sub>C0</sub>	$l_{\rm H_2O}^{-1}$ atm <sup>-1</sup> )	
k <sub>CO2,H2</sub> O	34.06	23.89	14.90	34
Electrochemic	al properties°			
	Т	hermoneutral po	otential (V)	
$U_{\text{th,CO}_2 \rightarrow \text{CO}}$	1.467	1.474	1.488	48
U <sub>th,CO<sub>2</sub>→C<sub>2</sub>H<sub>4</sub></sub>	1.219	1.222	1.229	48
$U_{\text{th},H_2O\rightarrow H_2}$	1.481	1.494	1.519	48

Relevant system properties for the system's heat sinks, salt formation, water management/ membrane and electrochemical properties.  $^{4}$ Solubility values for CsHCO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> are extrapolated from 15  $^{\circ}$ C via correlation to the respective KHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> temperature trends.  $^{5}$ Conductivity ( $\sigma$ ) values of Sustainion X37 in 1M KOH and 1M KHCO<sub>3</sub>, respectively.  $^{\circ}$ Thermoneutral potential ( $E_{\rm th}$ ) values of the global reaction assuming the oxygen evolution reaction at the anode.

which see a wider yield of  $C_1$  and  $C_2$  products due to the moderate binding energy of intermediate CO. Whereas limited datasets exist for testing copper at higher temperatures, experiments show that higher temperatures can result in increased selectivity towards carbon-based products versus hydrogen at a current density of 300 mA cm $^{-2}$ . The product distribution, however, shifts away from products such as ethylene and ethanol, leaving CO as the dominant product potentially due to the weakening of CO binding $^{9}$ . Thus, the desired optimal temperature is influenced markedly by the temperature-dependent selectivity towards the targeted products while a sufficient supply of CO $_2$  to the catalyst surface must be maintained.

An upside of higher temperatures is the increased solubility of (bi)carbonate salts, mitigating salt formation  $^{36}$ . Instead, however, we predict that water management from the anode to the cathode could become a new central challenge for  $CO_2E$ . Simulations indicate that  $H_2O$  availability at the cathode is a potential bottleneck for the system  $^{37}$ , whereas experiments highlight the  $C_{2+}$  selectivity effects of higher and lower water activities  $^{38}$ . At higher temperatures, the selectivity of membranes usually decreases due to enhanced swelling, implying

increased crossover of cations  $^{21,39}$ . Although the water delivery to the cathode catalyst layer should be easier, the flooding potential increases, combined with the decreasing capillary pressure of the gas diffusion electrode  $^{27}$ . In addition, the increased saturation level of the CO<sub>2</sub> gas and the higher water vapour pressure increases the danger of drying out if relative humidities are too low  $^{40}$ . Thus, without proper humidification one could see accelerated salt precipitation, despite the higher solubilities mentioned above. Furthermore, a drier membrane shows a lower conductivity and thus higher overpotentials  $^{19,39}$ .

These brief discussions highlight how sensitive  $\mathrm{CO}_2\mathrm{E}$  is to temperature, and thus how challenging it is to operate under optimal conditions. Depending on the scale of the present internal temperature gradient, spatial dependences can induce even higher complexity. The discussions above indicate that the optimal temperature within the operable temperature range will be application-specific, influenced by a multitude of phenomena and generally as high as possible before voltage advantages are overshadowed by limiting phenomena  $^{41}$ .

### Heat recuperation is key for high process efficiencies

We showed that heat must be removed directly from the stack or from the anolyte circuit (see Fig. 2a). Here we briefly show that heat recuperation through secondary processes has the potential to effectively increase the energy efficiency of  $CO_2$  electrolysers. To illustrate this point we can consider three cases that are representative but not exhaustive for scenarios dealing with the dissipated heat. For discussion, we assume that the dissipated heat from the electrolyser system is at 50 °C (see Fig. 4).

The base case 'W' represents the scenario in which the dissipated heat is not used and thus needs to be removed, requiring additional cooling costs. This results in an energy penalty and a process efficiency  $\eta_{\rm W}$  that is below the energy efficiency of the CO<sub>2</sub>E stack.

In a second scenario, labelled case 'A', the 50 °C waste heat is upgraded via a heat pump to 110 °C, giving it higher utility for industrial processes such as downstream separation. An additional power requirement  $P_{\rm A}$  for the heat pump is then needed, but the upgraded temperature results in recovery of the electrolyser system's heat, boosting the process efficiency. The increase in process efficiency  $\eta_{\rm A}$  depends on the efficiency of the heat pump, which generally decreases with an increase in the temperature gap  $\Delta T_{\rm HP}$  to be bridges by the heat pump  $^{42}$ . This case is representative of any process that needs heat input on a substantially higher temperature level than the operation temperature of the stack.

In the third scenario, case 'B', the dissipated heat is valorized directly with little to no upgrading. Here we take the example of district heating in the case where the CO<sub>2</sub>E stack is located next to a decentralized heating system. Consequently, the heat pump power requirement  $P_{\rm B}$ , if needed at all, is lower than  $P_{\rm A}$ , meaning that  $\eta_{\rm B}$  is greater than  $\eta_{\rm A}$ . For an exact quantification of the efficiency of the processes, the exit temperature levels for cases A and B need to be known. However, the above argumentation shows that a higher operation temperature of the stack generally benefits the heat recuperation. All in all, heat recuperation could increase the energy efficiency of the system substantially, if the CO<sub>2</sub>E stack is considered not only as a power sink and a production unit but also as a low-temperature heat source. We note that, in general CO<sub>2</sub>E, the heat utility will be low due to the absolute temperature limit of 100 °C. Heat recuperation is then more valuable and essential for alternative technological routes, for example, the reverse water-gas shift reaction or in solid-oxide electrolysers.

#### **Outlook**

Literature reports on  $CO_2E$  often discuss the need for scale-up and operating under industrially relevant conditions <sup>1,2,43</sup>. In this Perspective we stress that a component of these conditions is operating in the range of 40–70 °C. The field of  $CO_2E$  and especially the understanding

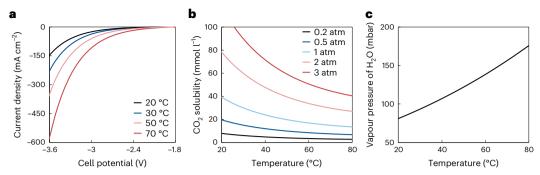
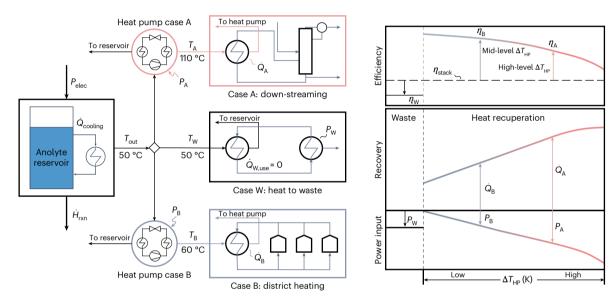


Fig. 3 | Effect of temperature on relevant system properties. a, Impact of temperature on the cell potential–current density curve of an MEA cell, showing faster kinetics with increasing temperature. Data from ref. 9. b, Solubility of  $CO_2$  in water as a function of temperature at different partial pressure levels of  $CO_2$ ,

indicating the increased mass transfer resistance regarding  $CO_2$  at elevated temperatures.  $\mathbf{c}$ , Vapour pressure of  $H_2O$  as a function of temperature, which indicates the potential danger of dry zones at elevated temperatures. Property data for  $\mathbf{b}$  and  $\mathbf{c}$  from refs. 9,22,34.



**Fig. 4** | **Heat recuperation and impact on achievable process efficiencies.** Heat that is dissipated from the CO<sub>2</sub>E stack, which has a power input  $P_{\rm elec}$  that is used partly for the generation of products governed by the reaction enthalpy rate  $\dot{H}_{\rm rxn}$  and is countered at the anolyte reservoir by the cooling heat duty  $\dot{Q}_{\rm cooling}$ , can be reused to enhance the process efficiency. Three use cases are depicted here. Case B represents district heating, as an example of processes that are on a similar temperature level  $T_{\rm B}$  as the heat duty temperature level  $T_{\rm out}$ . The efficient heat pumping, due to the low temperature gap ( $\Delta T_{\rm HP}$ ) that is to be bridged, brings a high process efficiency ( $\eta_{\rm B}$ ). Case A represents down-streaming, as an example of processes that are on a substantial higher temperature level  $T_{\rm A}$  compared with

 $T_{\rm out}$ . The process efficiency  $\eta_{\rm A}$  decreases in comparison with  $\eta_{\rm B}$  as the higher heat pumping requirement  $P_{\rm A}$  is not offset by the gain in the reusable heat transfer rate  $\dot{Q}_{\rm A}$  relative to the reusable heat transfer rate  $\dot{Q}_{\rm B}$  and the heat pumping requirement  $P_{\rm B}$ . Case W represents the absence of heat recuperation meaning the reusable heat transfer rate in case W ( $\dot{Q}_{\rm W,use}$ ) equals zero. The power penalty  $P_{\rm W}$  is imposed to meet the energy requirements for cooling down  $T_{\rm W}$ , which is equal to  $T_{\rm out}$ , leading to a process efficiency  $\eta_{\rm W}$  that is below the stack efficiency  $\eta_{\rm stack}$ . Any energy inputs or outputs, except  $\dot{Q}_{\rm A}$  and  $\dot{Q}_{\rm B}$ , within the district heating or down-streaming scenarios, are not part of the system balance displayed here.

of relevant phenomena in MEA cells is rapidly expanding, and shifting to testing at elevated temperatures prevents potential unwelcome surprises at the scale-up stage. Furthermore, the means of heat removal from a stack, via either the anolyte or integrated cooling channels, has implications for the design and operation of the electrolyser. Consequently, research areas such as flow field design and durability testing need to have heat management or higher temperature, respectively, in mind. In addition, modelling and in situ analysis, whose outcomes are temperature-dependent, should incorporate these assertions to better characterize a scaled-up  $\mathrm{CO}_2\mathrm{E}$  system  $^{30-32}$ .

A key aspect of the above reasoning is that the accessibility of performing research at  $40-70~^{\circ}\text{C}$  is important but non-trivial. Thousands of researchers are actively working in  $\text{CO}_2\text{E}$ , with a breadth of scientific backgrounds and access to equipment. Engineering systems with controlled and measurable temperature and  $\text{CO}_2$  humidities are then a very real barrier to shifting away from research under

ambient conditions. Ideally, these controlled set-ups include not only experimental electrolyser test benches but also in situ characterization methods as much as possible. Thus, we encourage the sharing of well-implemented higher-temperature testing set-ups across the community.

In summary, we argue that industry-scale  $\text{CO}_2\text{E}$  stacks will inevitably heat up, causing both predictable and unpredictable effects on efficiency, stability and operation. By incorporating these realities into our methodologies and hypotheses, it is hoped that we can shorten the development time from current laboratory scale to industrial application.

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The authors declare no competing interests.

#### **Additional information**

**Correspondence** should be addressed to Henri M. Pelzer or Thomas Burdyny.

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