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# Addressing challenges for operating electrochemical solar fuels technologies under variable and diurnal conditions

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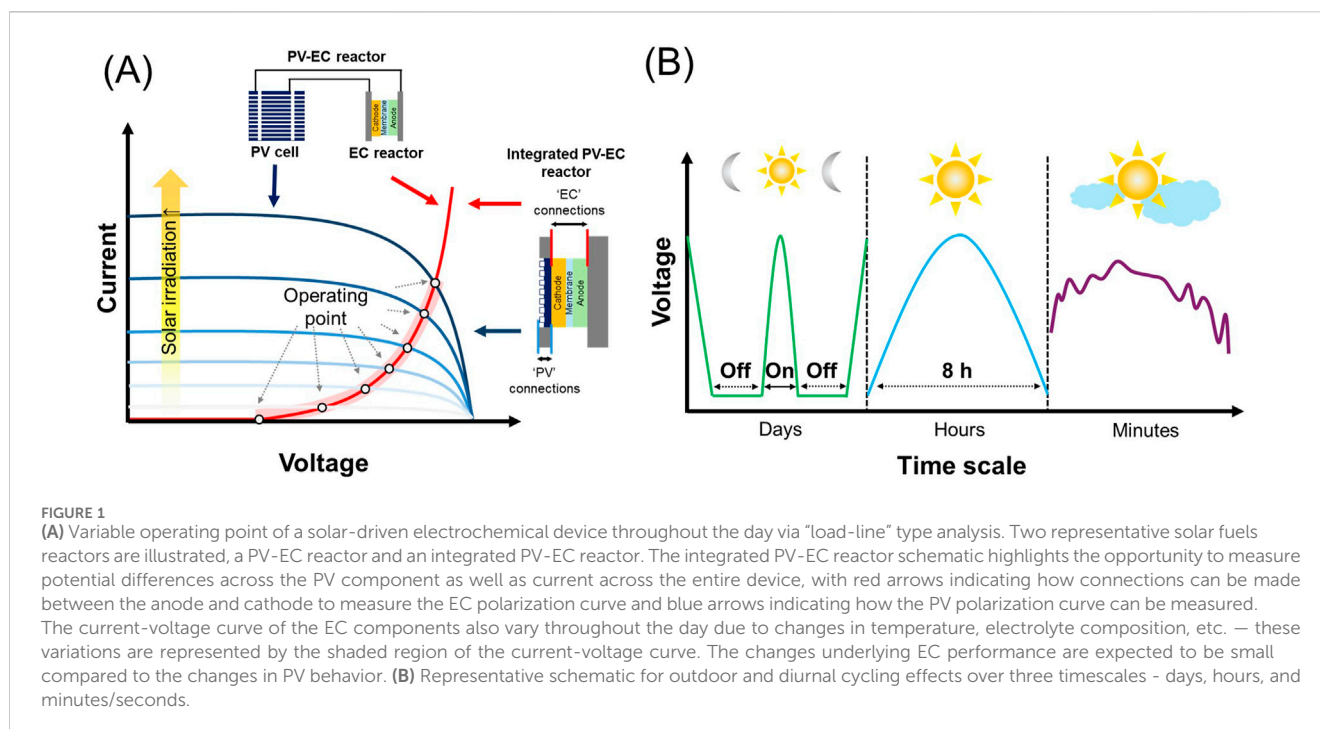
The outdoor operation of electrochemical solar fuels devices must contend with challenges presented by the cycles of solar irradiance, temperature, and other meteorological factors. Herein, we discuss challenges associated with these fluctuations presented over three timescales, including the effects of diurnal cycling over the course of many days, a single diurnal cycle over the course of hours, and meteorological phenomena that cause fluctuations on the order of seconds to minutes. We also highlight both reaction-independent and reaction-specific effects of variable conditions for the hydrogen evolution reaction and CO<sub>2</sub> reduction reaction. We identify key areas of research for advancing the outdoor operation of solar fuels technology and highlight the need for metrics and benchmarks to enable the comparison of diurnal studies across systems and geographical locations.

## KEYWORDS

solar fuels and chemicals, electrochemistry, durability, photovoltaics, hydrogen, CO<sub>2</sub> reduction, electrocatalysis

## Introduction

Solar-driven, electrified synthesis of chemical commodities, including H<sub>2</sub>, carbon-, and nitrogen-based chemicals from abundant feedstocks (e.g., H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>), is an area of substantial research interest (Agyekum et al., 2022; Ardo et al., 2018; Basic Energy Sciences Roundtable, 2019; Hisatomi et al., 2014; Kibria et al., 2019; Pareek et al., 2020; Wang et al., 2019; Xu et al., 2024). Integrated electrochemical solar fuels reactors offer a pathway for decarbonized chemicals production and modular, off-grid deployment (Grimm et al., 2020; Mishra et al., 2007). These reactors are defined by the integration of photo- and electrocatalytically active components through careful coupling and/or co-design of active interfaces. However, there are significant research challenges associated with the translation of these solar-driven reactors from operation under “static” laboratory operating conditions to the variable conditions that these devices must tolerate once deployed outdoors (Nandjou and Haussener, 2017). While this transition has been successful for



the photovoltaic (PV) industry, there remains a need to characterize the consequences of fluctuations inherent to outdoor, diurnal (i.e., the daily cycle of irradiation over a 24 h period) cycles to enable long-term, durable operation of integrated solar fuels systems.

The output of an electrochemical solar fuels reactor is a function of both photoactivity and electrocatalytic activity. While this concept is applicable to all types of electrochemical solar fuels reactors, it can be readily demonstrated in a photovoltaic-electrochemical (PV-EC) type reactor where the photovoltaic (PV) and electrochemical (EC) components can be characterized independently (Figure 1) (King et al., 2022; Wei et al., 2023; Yap et al., 2024b). The PV current-voltage curve is a function of multiple factors that dictate light-to-electricity conversion, including photon absorption, charge separation, and carrier transport (Moliton and Nunzi, 2006). The EC current-voltage curve captures the factors that dictate charge transfer across the electrode/electrolyte interface to produce fuels and chemicals, including the effects of catalytic activity, mass transport limitations, and ohmic losses (Gerhardt et al., 2021; Giordano et al., 2016). Under variable irradiation intensity and meteorological conditions (e.g., ambient temperature, wind, cloud coverage, irradiation spectra), both PV and EC polarization curves will vary (Figure 1A) (Faiman, 2008; Marion, 2002; van Dyk et al., 2005; Yap et al., 2024b). As a result, multiple operating points—up to and including a continuum of operating points—will arise for a solar fuels reactor throughout a diurnal cycle. Characterizing a representative subset of these operating points, especially those in which substantial changes to the structure and/or stability of photoactive or electrocatalytically active components occur, will be critical to the developing of solar fuels devices capable of matching the decades-long operating lifetimes already demonstrated for photovoltaics operating outdoors. The performance of other solar fuels devices, such as

photoelectrochemical (PEC) devices that include direct semiconductor/electrolyte interfaces or photocatalytic (PC) systems in which the light absorber is nanoparticulate or molecular, will also be strongly affected by variable conditions. These present additional, important research challenges to disentangle the effects of diurnal cycling on photo- and electrocatalytic performance.

While the fluctuating conditions encountered in outdoor operation are complex and interrelated, we highlight three timescales on which to evaluate them: days, hours, and minutes/seconds. Over days, a solar fuels reactor must be able to maintain its performance (i.e., the activity, selectivity, and durability of the device over time) throughout many repetitions of cycling between operation during the day and "off" conditions at night (Datta et al., 2023). The "off" condition is defined as the state of operation for the solar-driven reactor where no, or nearly no, photo-driven response occurs. On the scale of hours, the operation of the solar fuels reactor will vary with incident solar irradiance as well as changes in meteorological conditions (e.g., changes in ambient temperature, humidity) — the hours of greatest solar irradiance will generally result in operation at points with greater power and total product output (Yap et al., 2024b). Finally, on the order of minutes/seconds, additional meteorological effects, such as dynamic cloud coverage and shading from surroundings, will cause fluctuations in the operation of the solar fuels reactor (Aly et al., 2019; Yap et al., 2024b; Ye et al., 2013). The fluctuations on these different timescales have distinct effects on solar fuels reactors and require the design of systems capable of maintaining selectivity, activity, and durability under variable conditions.

Efforts have been made to understand diurnal-driven effects for both the solar-driven electrochemical H<sub>2</sub> evolution reaction (HER) and the CO<sub>2</sub> reduction (CO<sub>2</sub>R) reaction. For example, GaInP<sub>2</sub>/GaAs|MoS<sub>2</sub> photoelectrodes designed to drive HER were tested

outdoors in Golden, Colorado over single daylight periods (i.e., <12 h) and exhibited gradual loss of H<sub>2</sub> production throughout the day (Ben-Naim et al., 2022). These conditions, where the reactor is illuminated by the sun, are often referred to as “on-sun” conditions (in contrast to simulated conditions in a laboratory). SrTiO<sub>3</sub>:Al photocatalyst sheets were scaled to 100 m<sup>2</sup> and operated outdoors for several months, achieving a maximum solar-to-hydrogen efficiency of 0.76% (Nandy et al., 2023; Nishiyama et al., 2021). Other efforts have assessed extended cycling stability (12 h/12 h) for HER systems for metal|oxide|semiconductor Si and tandem III-V photoelectrode architectures (Bae et al., 2019; Walczak et al., 2017). For CO<sub>2</sub>R systems, durability studies have been conducted operating at a single illumination intensity (e.g., 1000 W m<sup>-2</sup>) for over 10 hours with on/off cycling (Cheng et al., 2020; Gurudayal et al., 2019; Kamata et al., 2021; Kato et al., 2021a; Kato et al., 2021b; Kistler et al., 2021). Additionally, existing solar-driven CO<sub>2</sub>R studies probing diurnal performance have investigated operation under idealized conditions (e.g., assuming no loss of performance) via computational methods, with a focus on selectivity (King et al., 2022; Yap et al., 2023; Yap et al., 2024b). However, substantial advancements in durability as well as overall performance under outdoor operation (e.g., solar-to-fuel conversion efficiency > 10%) are still needed for electrochemical solar fuels to become a competitive technical solution (Haussener, 2022).

Herein, we consider the effects of fluctuating, diurnal conditions expected during outdoor operation of electrochemical solar fuels reactors across three timescales (days, hours, minutes/seconds) and with respect to both reaction-independent and reaction-specific effects. Reaction-independent effects refer to those which must be considered for any electrochemical solar fuels reaction, in contrast to reaction-specific effects associated with unique challenges which arise for individual reactions of interest (e.g., HER, CO<sub>2</sub>R, etc.). We also consider the role of reactor design engineering to optimize solar fuels performance with respect to diurnal conditions and highlight areas of research which can advance solar fuels technology. This work seeks to address the challenge of stable, selective electrochemical solar fuels systems under fluctuating conditions by providing a roadmap of potential focus areas for future solar fuels research.

## Reaction-independent considerations for outdoor testing and diurnal cycling

Variations in light intensity/spectrum and temperature, which are a function of the local meteorological climate and geographical location, will exert influence on any solar-driven process.

During outdoor operation, variable irradiation drives changes in the operating point of the solar fuels reactor, causing variations in current flows and electrochemical potential differences across key interfaces (e.g., catalyst/electrolyte, electrolyte/membrane, catalyst/membrane, etc.) (Figure 1). For multiday, diurnal operation, cycling between illuminated (termed “on” for simulated illumination, or “on-sun” for outdoor illumination) and dark conditions at night (termed “off”) will affect the performance of all solar-driven devices. These on/off changes can substantially impact the stability of the electrochemical components. For example, in membrane electrode

assembly (MEA) reactors, on/off cycling can affect ion transport properties across the membrane and separation efficiency of product species, resulting in loss of performance over the course of many cycles (Jao et al., 2011; Péron et al., 2008). At the (photo) electrode interface, periods under “off” conditions can result in corrosion of the electrocatalyst due to the formation and instability of surface oxide species — this is also relevant for the semiconductor in PEC/PC systems with semiconductor/electrolyte interfaces. The thermodynamics of such changes in stability should be evaluated and can often be understood in the context of an appropriately constructed Pourbaix diagram. Importantly, the nature of the device’s “off” condition should also be carefully considered. For example, a reactor at night may tend toward an “open-circuit” type condition, where no net current flows through the system, or a “reversed-current” condition depending on reactor design, electrolyte composition (e.g., concentration of dissolved redox-active species like H<sub>2</sub> and O<sub>2</sub>) and electrode structure (Collins et al., 2024; Fu et al., 2020; Weiß et al., 2019). Studying the consequences of extended “off” periods on performance, such as at open-circuit, will be essential to designing solar-driven systems that are stable over the course of many diurnal cycles. To mirror the standard outdoor measurement protocols for PVs (Khenkin et al., 2020), experiments to isolate and evaluate device day/night durability over multiple cycles will be valuable and may involve cycling between different electrochemical potentials (e.g., expected peak current and open-circuit) over many cycles on timescales similar to those expected during diurnal operation (e.g., 12 h on/12 h off, 16 h on/8 h off). Shorter experiments, conducted using a potentiostat or solar simulator equipped with a light shutter, could be employed to evaluate stability during day/night cycling, but developing mechanistic connections between any accelerated diurnal cycling methodology and the full 24 h timescale of a true diurnal cycle will be critical.

Throughout a single diurnal cycle (i.e., 1 day), solar irradiation changes over the course of hours and is dependent on seasonal, locational, and other environmental factors. Since it is difficult to directly compare the “on-sun” performance of solar fuels devices at different locations, most solar fuels reactors have been evaluated under illumination at 1000 W m<sup>-2</sup> (i.e., 1-sun) with a fixed AM 1.5G spectrum. This translates to operation of the solar fuels device at a single operating point (Cheng et al., 2020; Kuang et al., 2019; Pan et al., 2023; Yap et al., 2024a). However, estimating a diurnal output from constant illumination conditions can result in overestimations of performance and can fail to capture the consequences of diurnal variation in incident solar spectrum on effects such as carrier collection, solvent absorption, and PV heat absorption (Ishii et al., 2013; Kistler et al., 2020; Nofuentes et al., 2014). Ambient temperature, which can vary significantly over a day, as well as across locations and seasons, will also dictate changes in performance and durability. At low operating temperatures (e.g., at night or during the winter), ion transport rates decrease. This can decrease conductivity, slow ion transport, and cause deformation of membranes, resulting in expedited degradation of performance in the electrochemical device (Guo and Qi, 2006; Kim and Mench, 2007). Designs and studies that consider these temperature-driven phenomena, and the effects of cycling between freezing and thawing, will be key to building temperature-robust solar fuels devices (Mensharapov et al., 2022; Shengsheng, 2006).

Where enabled by device design, testing varying potential conditions that mimic those expected under the hourly diurnal irradiation profile can be used to experimentally probe the hours-scale stability of solar fuels devices. These potential profiles will be unique to each solar fuels setup and are dependent on the operating points described in Figure 1. To accurately simulate these profiles, it is valuable to measure both current across the device as well as voltage across the photoactive component (where possible) (Figure 1A) for the device in question from outdoor testing — this data is useful in assigning performance drops to specific components of the solar fuels reactor (Kistler and Agbo, 2020). It is useful to recognize that there may be multiple mechanisms of degradation in solar fuels devices, including some that may occur under illuminated conditions without requiring “on/off” cycling. Probing these degradation mechanisms over multiple cycles, without a simulated “off” state can elucidate the stability of the solar fuels device with respect to hourly changes, and the reversibility of any changes which may occur in the electrocatalyst (e.g., oxidation or electronic state changes, morphology changes) (Hochfilzer et al., 2023; Minguzzi et al., 2012). Recent work to investigate the durability of GaInP-based photocathodes for HER has emphasized the importance of operating conditions and photoelectrode design, highlighting the competition between charge transfer towards product formation versus degradation, and the need to control the movement of electrons and holes to dictate long-term durability, even when the photoelectrode is maintained under reducing and/or oxidizing conditions (Yu et al., 2021). Additionally, diurnal spectral variation and changes in temperature of the PV or EC components (due to ambient temperature and/or irradiation-driven heating) can be monitored and studied separately in a controlled lab environment — these efforts combined with varying applied potential could be used to simulate “on-sun” experiments.

The U.S. Department of Energy’s (DOE) protocol (Bloom et al., 2013; Yuan et al., 2011) for polymer-electrolyte membrane fuel cells (PEMFC) provides inspiration for durability testing of solar fuel devices under variable conditions, including steady-state durability tests, potential cycling durability tests, and start-up/shutdown cycling durability tests. Of particular applicability to solar fuels devices are load cycling tests with conditions spanning from minimum to maximum operating current/potential for the solar fuels device. When coupled with *in-situ* characterization techniques, such as online inductively-coupled plasma mass spectroscopy (ICP-MS) (Ji et al., 2020; Ledendecker et al., 2017), these tests can provide insight into the stability of the electrochemical components under conditions representative of those expected during on-sun operation.

Variations caused by meteorological and environmental fluctuations, such as cloud coverage, rain, shade, and wind, result in changes in the operating conditions of solar fuels devices on the second-to-minutes scale (Figure 1).<sup>30</sup> Potential step methods with various step frequencies and applied potentials, or illuminated experiments with light chopping at various frequencies, can be employed to probe the consequences of meteorological fluctuations. Degradation studies in battery science provide insight into possible failure modes under these conditions — degradation mechanisms of Li-ion batteries under accelerated stress test conditions include electrode structural change and

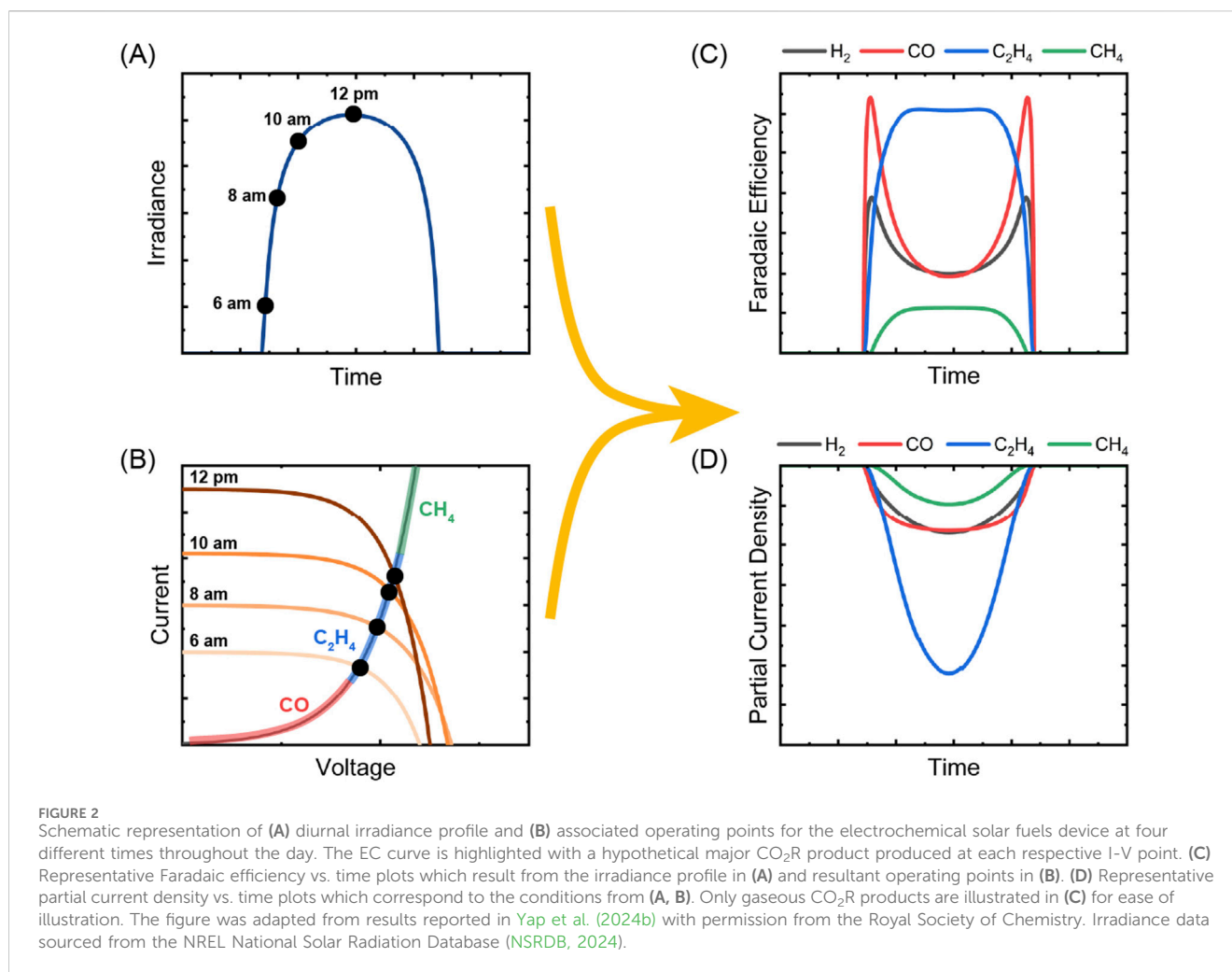
decomposition, particle fracture, solid-electrolyte interface growth and Li plating (Edge et al., 2021; Liu et al., 2022; Pender et al., 2020; Xiong et al., 2020; Zhu et al., 2020). Mirroring these battery degradation mechanisms, one significant challenge that may be associated with short-term fluctuation in conditions is catalyst degradation due to volume change or phase change, resulting in catalyst leaching (Bae et al., 2019). If the catalyst has multiple chemical states, or a small potential window in which it is stable, meteorological fluctuations may be a critical driver of degradation. Solar fuels systems will require the development of electrode structures, including the support, catalyst, and any protective overlayers, which are able to maintain their performance within a wide operating window.

## Reaction-specific considerations for outdoor testing and diurnal cycling

Reaction-specific considerations pertaining to solar-driven HER and CO<sub>2</sub>R under variable conditions and diurnal cycles are also important to consider. These include selectivity variations for single product vs. multi-product electrochemical reactions as well as temperature changes throughout the diurnal cycle.

For reactions expected to produce a single product, such as HER, the product formation rate is expected to scale proportionally with the irradiance profile. In these cases, the challenge is to maximize product output per day (i.e., charge passed per day) and to maintain performance over the course of many days. For electrocatalysts that can be tested in isolation from photoactive components, these conditions could be simulated by well-designed potential profiles to sweep from “off” condition potentials to those that mimic the irradiation profile, followed by an extended hold at ‘open-circuit’ or under relevant “reversed-current” conditions to simulate the “off” period. Developing electrochemical systems able to maintain this performance over repeated on/off cycles would be a valuable step toward solar fuels systems capable of operating under outdoor and diurnal conditions for lifetimes similar to those of the PV component. Such advances would also benefit electrochemical systems, improving energy efficiency and tolerance to changes caused by fluctuations in local microenvironment conditions.

Multi-product electrochemical reactions, such as CO<sub>2</sub>R using a Cu-based catalyst, have product distributions (e.g., C<sub>2</sub>H<sub>4</sub>, EtOH, CH<sub>4</sub>, CO, H<sub>2</sub>, etc.) which are highly dependent on applied potential and features of the catalyst/electrolyte interface (Garza et al., 2018; Huang et al., 2019; Lv et al., 2018; Nitopi et al., 2019; Todorova et al., 2020). The CO<sub>2</sub>R product distribution is affected by the properties of the local microenvironment, including the structure of the electric double layer, pH, temperature, and catalyst morphology/active sites (Bui et al., 2022; Pan and Yang, 2020; Simon et al., 2021; Sun et al., 2020; Zhang et al., 2020). In solar fuels systems, the additional variability expected during outdoor operation introduces distinct performance considerations. The nature of the irradiation profile (Figures 2A, B) will result in the formation of variable electrochemical potential differences — in a PV-EC-type device this is readily represented by changes in operating point (i.e., full cell voltage and total current) throughout the day. For multi-product CO<sub>2</sub>R systems, this translates to varying product distributions and periods when different CO<sub>2</sub>R products will dominate (e.g., CO,

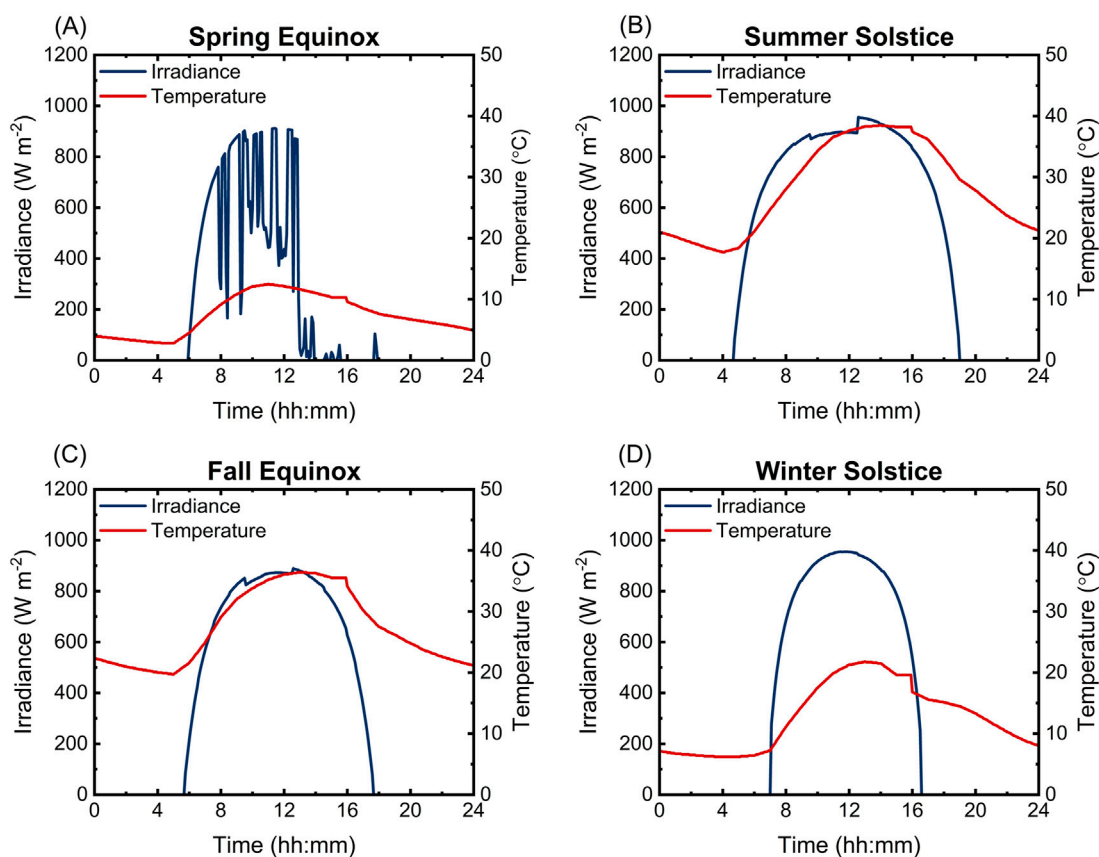


C<sub>2</sub>H<sub>4</sub>) (Figures 2C, D). The extent to which product output ratios (e.g., CO:H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>:CH<sub>4</sub>) differ between low and high irradiation windows is dependent on the potential range in which the electrocatalyst can maintain similar product selectivity. For example, using a Cu electrocatalyst, modeling has suggested that CO and H<sub>2</sub> will be favored at times of lower irradiation and products such as C<sub>2</sub>H<sub>4</sub> will be favored during higher irradiation periods (Figure 2C) (Garza et al., 2018; Todorova et al., 2020; Yap et al., 2024b). Electrocatalysts capable of demonstrating the desired selectivity in wide potential windows are important for improving tolerance to fluctuating irradiation conditions and can minimize the extent to which downstream processes (e.g., separation or further reaction) will have to adapt to variations in the product stream. Fluctuating conditions are also important in CO<sub>2</sub>R systems designed to produce CO (e.g., those using Au, Ag-based cathodes), and recent work has highlighted the opportunity for stable Ag-based CO<sub>2</sub>R MEA systems over many cycles (Samu et al., 2022).

The diurnal irradiation cycle is accompanied by a variable ambient temperature profile (Figure 3). Ambient temperature, combined with irradiation-derived heat adsorption, defines the operating temperature of both PV and EC components when left unregulated. While these temperature effects are well-studied for commercial-grade PVs (Faiman, 2008), the consequences of these phenomena on integrated solar-driven electrochemical systems

remain an important question. For example, current, state-of-the-art water electrolyzers utilize proton exchange membranes (PEM) or anion exchange membranes (AEM) and operate at 80°C (Aili et al., 2023; Corti, 2022; Ion-Ebrasu et al., 2020; Ion-Ebrasu et al., 2020; Lee et al., 2023). If a solar fuels system uses a similar membrane-containing architecture, fluctuations in temperature are likely to have consequences on activation, ohmic, and diffusion overpotentials, and have potential consequences on the stability of even the most durable membranes commonly used in these electrolyzers (Chandesris et al., 2015; Guo and Qi, 2006; Kim and Mench, 2007; Okonkwo et al., 2021; Olivier et al., 2017; Yigit and Selamet, 2016).

Temperature changes can influence selectivity, activity, and durability of the reactor. For conventional CO<sub>2</sub>R systems, temperature changes can affect the solubility of CO<sub>2</sub> in the electrolyte, resulting in changes of the interfacial pH, selectivity, and activity (Vos et al., 2023; Vos and Koper, 2022). Additionally, in multi-product mechanisms, different products may have different temperature dependence, resulting in selectively profiles that are a complex function of temperature (Vos et al., 2023; Vos and Koper, 2022; Yap et al., 2024b). This temperature dependence can also vary as a function of the characteristics of the catalyst/electrolyte interface, adding to the complexity of temperature cycling in multi-product systems (Corpus et al., 2023; Weng et al., 2018).



**FIGURE 3**  
Irradiance vs. time and ambient temperature vs. time profiles for Barstow, CA for 4 days in 2020. A representative day for each season was chosen. Data is sourced from NREL's National Solar Radiation Database (NSRDB, 2024). (A) Spring equinox. (B) Summer solstice. (C) Fall equinox. (D) Winter solstice.

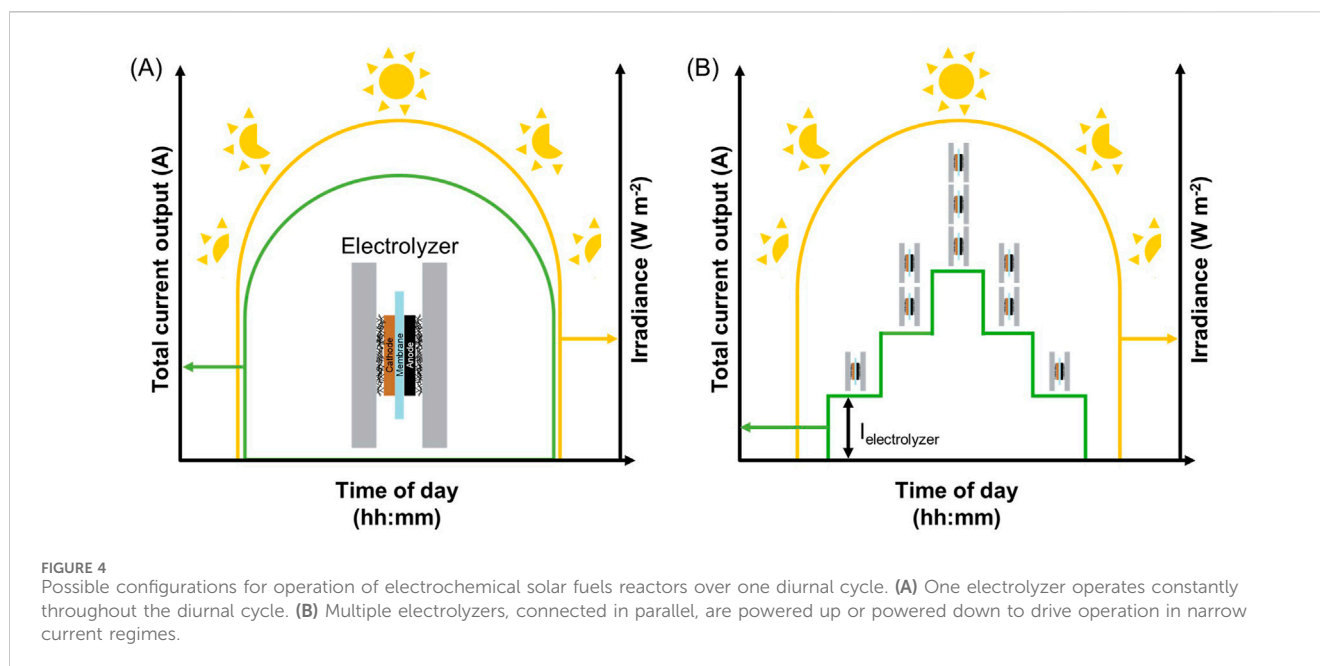
The temperature dependence of CO<sub>2</sub>R product output remains an important question and should be answered in controlled electrochemical environments to inform diurnal operation. Finally, in CO<sub>2</sub>R systems, AEM are commonly used to favor CO<sub>2</sub>R over the competing HER (Salvatore et al., 2021). The development of AEMs is an active field and the choice of AEM directly influences the selectivity of CO<sub>2</sub>R systems through changes in OH<sup>-</sup> conductivity, pH stability, and temperature tolerance (Luo et al., 2020; Salvatore et al., 2021; Yin et al., 2019). The chemical and mechanical stability of AEMs in CO<sub>2</sub>R-specific environments is a key concern, and a solar-fuels compatible AEM must exhibit a wide temperature stability range and be able to withstand short-term variations in ionic current, electric field, and pH under diurnal conditions (Krivina et al., 2022; Lindquist et al., 2021; Salvatore et al., 2021).

## Reactor design configuration and engineering

Reactor design will also be key toward optimizing outdoor, diurnal operation. Optimizing this design at the lab-scale will enable smoother transition to larger-scale systems and can provide resilience against changes in operating temperature,

irradiation, or other environmental factors. Utilizing heat available from “on-sun” operation presents an opportunity to integrate heating/cooling in innovative and distinct ways to improve overall energy efficiency (Kempainen et al., 2023; Kistler et al., 2022; Kölbach et al., 2022; Tembhrne et al., 2019; Tembhrne and Haussener, 2019). Additionally, a more complete utilization of the solar spectrum (e.g., low energy photons) can allow for thermal coupling of irradiation and electrocatalytic activity, improving the efficiency of the solar fuels reactor (Johnson and Haussener, 2024). Integrated solar fuels reactors also offer the unique opportunity to utilize generated heat for potentially beneficial hybrid technology, including thermally-driven conversion of H<sub>2</sub> into higher value products, such as green ammonia (Tembhrne and Haussener, 2016). Designing and modeling heat integration systems under simulated diurnal conditions will improve energy efficiency when scaling electrochemical solar fuels reactors beyond the lab scale and identify ways to reduce capital (CapEx) and operating (OpEx) costs.

Another important consideration in scaling of solar fuels systems is the operating configuration. In a PV-EC architecture, for example, there is an opportunity to control product output and efficiency through plant design, as illustrated in Figure 4. In one configuration, an electrolyzer operates without any additional power regulation (Figure 4A). This results in a variable product generation



rate (represented by current output) throughout the diurnal cycle that may add complexity in downstream separation processes. In the other, multiple electrolyzers are employed, where additional electrolyzers, connected in parallel, are turned on only after a particular power threshold (as defined by the current-voltage profile and associated selectivity) is reached (Figure 4B). This configuration will result in lower power efficiency and individual electrolyzer capacity factor, but may reduce the complexity and cost of the downstream separation processes. For a single product reaction, the first configuration may be advantageous to maximize total product output. Conversely, the second configuration may be more compatible with multi-product reactions where consistent product streams will lower separations costs. Designing the appropriate reactor for solar-driven fuel formation will require further technoeconomic studies to balance electrolyzer cost versus the cost of downstream separation.

## Key areas of research for outdoor solar fuels device operation

Understanding the performance of electrochemical solar fuels reactors under fluctuating, outdoor, diurnal conditions will be important in advancing the field. To tackle the reaction-specific challenge of selectivity during diurnal cycling, catalysts for multi-product reactions with high selectivity for a desired product over a wide range of potentials are needed (Chen et al., 2021; Lim et al., 2023). Coupled with the careful design of photoactive components, this can mitigate variations in the composition of the outlet product stream during daytime operation and reduce the downstream costs of product separation. To promote long-term cycling stability, reports on durability of existing and novel electrocatalysts under outdoor-like and cycling conditions are encouraged. Potential methods for evaluating this stability include coupling *in-situ* characterization techniques, such as online ICP-MS, to longer

electrochemical measurements which more accurately represent a full 24 h diurnal cycle (Pishgar et al., 2021; Popović et al., 2020). Identifying electrocatalytic changes which occur as potential is cycled is a crucial first step to designing durable catalysts and informing the design of appropriate “off” conditions for solar fuels devices. To enable comparison of various electrocatalysts under simulated outdoor conditions, there is a need to develop standardized durability testing methods representative of these conditions, focusing both on voltage changes and temperature changes driven by meteorological effects — these methods should address all three diurnal timescales (days, hours, and minutes/seconds). Similar experiments should also be conducted with temperature cycling to gain insight into the role of temperature on performance stability and to identify failure mechanisms under isolated conditions of potential and temperature cycling (Garbe et al., 2021; Tomić et al., 2023). Electrochemical systems designed for stability under these isolated potential and temperature conditions can then be advanced to outdoor performance tests.

Another critical aspect for the future outdoor, diurnal operation of solar fuels devices is the need to define standardized metrics and benchmarks to enable comparison across studies. Of particular importance are the parameters for evaluating electrocatalysts and membranes under the experimental regimes detailed above. For example, stability could be reported in relative values of loss (e.g., % activity loss over  $n$  cycles, % catalyst loss over  $n$  cycles) to remove differences derived from variable initial electrochemical systems [e.g., different catalyst loading, electrochemical active surface area (ECSA)] (Edgington and Seitz, 2023; Lopes, 2023). Another metric that must be considered for diurnal operation is diurnal solar-to-fuel conversion efficiency. Under outdoor, diurnal conditions, this calculation is complicated by changes in temperature, illumination, selectivity, and activity. Thus, there is a need to develop standardized methods for analyzing and comparing solar fuels performance across studies, as exists for PV systems (Kratochvil et al., 2004).

## Conclusion

The design and performance of electrochemical solar fuels systems must necessarily reflect the outdoor, diurnal conditions in which they will operate. We have identified three timescales of relevance for to outdoor operation and diurnal cycling (days, hours, and minutes/seconds) and discussed the challenges which arise with each of these timescales from the perspective of reaction-independent and reaction-specific challenges. To design solar fuels systems capable of maintaining performance outdoors over diurnal cycles, it is crucial to understand the operation constraints imposed by this variability and to design electrochemical and photovoltaic components, as well as reactors, which are capable of withstanding fluctuating conditions. A well-engineered solar fuels system must be designed to manage its own circadian rhythm, much like a biological organism, to properly respond to changes in external conditions and to maintain performance dynamically over long timescales. The challenge of stable outdoor operation must be addressed for deployable solar fuels technologies to become reality, and the advances driven by this research should be mutually beneficial to a range of electrochemical systems.

## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

## Author contributions

KY: Conceptualization, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing–original draft, Writing–review and editing. SL: Conceptualization, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing–original draft, Writing–review and editing. TK: Conceptualization, Validation, Writing–review and editing. DC:

Conceptualization, Validation, Writing–review and editing. EW: Conceptualization, Funding acquisition, Supervision, Validation, Writing–review and editing. HA: Conceptualization, Funding acquisition, Supervision, Writing–review and editing. TJ: Conceptualization, Funding acquisition, Supervision, Writing–review and editing. CX: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing–review and editing. AN: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing–original draft, Writing–review and editing, Methodology.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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