Perspective

Electrochemical methane production from CO₂ for orbital and interplanetary refueling

Stafford W. Sheehan

SUMMARY

Renewable CO₂ electrosynthesis is a potentially promising tool to utilize unwanted greenhouse gas. The greatest barrier to its adoption is rendering the production of CO₂-derived chemicals cost-competitive, such that they have higher net value than their fossil-derived equivalents. Among the commodities that have been made using CO₂, H₂O, and electricity, CH₄ is one of the simplest and most researched products. Technoeconomic studies of CO₂ methanation make it clear that its high-value applications are limited without significant subsidy on Earth, where it competes with low-cost natural gas. In space, however, CO₂ methanation via the Sabatier reaction is already used on the International Space Station to recycle atomic oxygen, and propulsion systems employing cryogenic liquid methane are in development for reusable rocket engines. Comparative analysis of power-to-gas using either CO₂ electrosynthesis or the Sabatier reaction from an aerospace perspective identifies research priorities and parameters for deployment. Given its atmospheric CO₂ concentration over 95%, Mars may present future opportunities for technology that could also help overcome our climate challenges on Earth.

INTRODUCTION

The reversal and prevention of anthropogenic climate change alongside rapid technological advancement in the modern era is among the greatest hurdles that humanity must overcome (Hoegh-Guldberg et al., 2019). Carbon dioxide (CO₂) is one of the most abundant greenhouse gases causing climate change and is a byproduct of biological and combustion processes. CO₂ is a critical component of our atmosphere and provides carbon as one of the building blocks for all life on Earth; therefore, a small amount of CO₂ in the air is necessary. However, burning fossil fuels has emitted an excess of CO₂ that has increased its atmospheric concentration to levels that have not been seen in the last 800,000 years (Lüthi et al., 2008). At the present concentration (>410 ppm) the rate that the earth is increasingly trapping heat produced by solar irradiation has extreme and far-reaching consequences that damages global ecosystems (Trisos et al., 2020), reduces biodiversity (Warren et al., 2018), alters weather patterns (Nangombe et al., 2018), and impedes humanity’s survivability (Jacobsen et al., 2019).

Beyond Earth, the atmosphere of Mars contains CO₂ with a much higher concentration, at over 95% (Franco et al., 2019). The high cost of transporting material from Earth to Mars necessitates utilization of resources in situ on Mars to produce materials and fuel required for habitation and further travel. The reusability of rocket engines that use liquid methane as fuel suggests that deployment of propellant depots in Earth orbit, on Mars, and elsewhere in the solar system may facilitate space travel in the future (Musk, 2017). This makes CO₂ conversion promising as an approach not only to fight climate change on Earth but also to enable interplanetary exploration. Applications on Earth and in space require much of the same technical development to enable efficient chemical manufacturing using CO₂ as a building block with renewable generated electricity.

Electricity generation and the chemical industry currently generate a substantial amount of CO₂ by burning fossil fuels (Katelhon et al., 2019). Over the past few decades, major efforts have been made toward utilization of renewable sources of electricity as an alternative. As such, the cost of solar and wind energy has decreased substantially, making renewable technologies more accessible at the grid-scale. The rate of renewable adoption in the electrical grids of developed countries is, thus, increasing rapidly (Mitchell, 2016). The chemical industry has not seen as rapid development and remains a major source of CO₂.
emissions to be addressed, and researchers are actively developing pathways for more sustainable chemical production to reduce its greenhouse gas emissions (Zimmerman et al., 2020).

One of the most widely studied pathways for both more sustainable chemical processes and production in space is electrification, in which the energy required for chemical production comes from electricity rather than chemical energy from fossil fuels. Although renewable energy infrastructure deployment is still a limiting factor, three practical advantages stand out to motivate its realization: (1) electrification allows for chemical production using renewables; (2) it enables new strategies for tackling the intermittency inherent in solar and wind energy; and (3) it couples chemical cost with the cost of electricity, which is projected to decrease with increasing renewable deployment (Blanco and Modestino, 2019). Furthermore, within electrification schemes, value-added C$_2$+ products are thermodynamically favored at lower temperatures (<250°C), whereas thermocatalytic activation of CO$_2$ requires higher temperature (Prieto, 2017). Electrosynthesis yields potential pathways to bridge this gap between thermodynamics and reaction kinetics for high-value products.

Although there are several pathways for producing chemicals and fuels using electrosynthesis, one of the most promising is electrosynthesis using CO$_2$ and H$_2$O starting materials with oxygen as a byproduct. This approach is undoubtedly compatible with Earth’s global atmospheric chemistry, with reactants, products, and energy sources that mimic photosynthesis but with higher energy conversion efficiency (Gonzalez Hernandez and Sheehan, 2020). On Mars, it is the only option for in situ resource utilization (ISRU) to produce organic products because CO$_2$ and H$_2$O are both present in large quantities (Barnes et al., 2020). There are several component technologies that enable chemical production from air, water, and sunlight, including single-step direct CO$_2$ electroreduction. In this case, reactant protons and electrons are liberated from water at an anode, which produces oxygen gas as a byproduct. At a cathode, CO$_2$ is combined with the protons and electrons to form a reduced carbon product. The process can be powered by renewable electricity (Chen et al., 2018). Another promising approach is the production of green H$_2$ and O$_2$ by water electrolysis powered by renewables, followed by hydrogenation of CO$_2$ to synthesize a product such as CH$_4$ or CH$_3$OH (Sarp et al., 2021). Although these are two of several examples of artificial photosynthesis, many others exist that may be useful in the future, including direct photocatalytic and photoelectrochemical approaches (Wang et al., 2019), microbial CO$_2$ conversion powered by renewable chemical energy (Dessi et al., 2021), and multi-step approaches where CO$_2$ is electrochemically converted to CO that is then used for downstream thermochemical production (Smith et al., 2019).

Although major benefits to using CO$_2$ as a feedstock material for chemical production are its potential to remove greenhouse gas from the atmosphere together with its presence on Earth, Mars, and inhabited space stations (from metabolic production), there are challenges to economic utilization (Zimmermann and Schomacker, 2017). A major constraint that limits the deployment of CO$_2$ utilization technologies is high production cost versus a typically lower-cost fossil-based incumbent on Earth (Spurgeon and Kumar, 2018). For this reason, when deploying CO$_2$ utilization technologies including those that use electrosynthesis to transform CO$_2$ into a value-added chemical, it is critical to target a high-value application rather than attempt to compete solely on a cost basis with an incumbent production method that utilizes low-cost fossil fuels. Common compounds that can be produced from CO$_2$, H$_2$O, and renewable electricity include carbon monoxide (CO), formic acid (HCOOH), methane (CH$_4$), methanol (CH$_3$OH), ethanol (CH$_3$CH$_2$OH), and ethylene (C$_2$H$_4$), and for each there are scenarios where additional value can be derived with electrosynthesis (Chen et al., 2018).

Among these CO$_2$-derived compounds, CH$_4$ has the lowest average market price as it is the major component of natural gas, which has an October 2020 industrial price of $0.15 per kilogram in the United States (U.S. Energy Information Administration, 2020). Technoeconomic assessment literature notes CO$_2$-derived CH$_4$ as one of the more challenging products made from reduced CO$_2$ to be competitive on a cost basis (Orella et al., 2020). In CO$_2$ methanation and power-to-gas technoeconomic assessments the cost is typically over $4.00 per kilogram; thus there is reliance on subsidy or low-cost hydrogen with few examples of economic deployment (Peters et al., 2019; Becker et al., 2019). However, there are use cases where CH$_4$ production from CO$_2$ does still provide significant value. In this perspective, I analyze the production of CH$_4$ from CO$_2$ by electrochemical and thermochemical methods for aerospace applications, including its current use to recycle atomic oxygen on the International Space Station (ISS) and future potential as a method to produce propellant for reusable rockets on Earth, in orbit, and on Mars.
ABITIC METHODS FOR METHANE PRODUCTION FROM CO₂

At a high level, there are two abiotic methods that can be used to produce methane from carbon dioxide, water, and electricity. In the direct electrochemical scheme, the cationic CO₂ electroreduction half-reaction is coupled with a corresponding half-reaction that provides the requisite protons and electrons to form CH₄. Equations 1 and 2 show this half-reaction in an electrochemical cell operating under acidic or basic conditions, respectively, and their corresponding potential versus the reversible hydrogen electrode (RHE).

\[
\begin{align*}
\text{CO}_2 + 8H^+ + 8e^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E_0 = 0.169V \text{ vs. RHE} \quad \text{(Equation 1)} \\
\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- &\rightarrow \text{CH}_4 + 8\text{OH}^- \quad E_0 = 0.169V \text{ vs. RHE} \quad \text{(Equation 2)}
\end{align*}
\]

Protons and electrons are typically provided by the water oxidation half-reaction but can also come from oxidation of waste organics generated by other life support or biological processes, resulting in a lower net cell voltage (Na et al., 2019). When the protons and electrons are provided by water oxidation (\(E_0 = 1.229 \text{ V versus RHE}\)), the thermodynamics of the process bears some similarities to hydrogen generation, in that the net reaction requires 1.06 V of electric potential to proceed at 25°C, which corresponds to 5.16 MWh per ton of CO₂ reacted (Haynes, 2014). This electric energy requirement corresponds to the Gibbs free energy of CH₄ formation from H₂O and CO₂. However, its use disregards the temperature-dependent thermal energy required to overcome reaction entropy. On the other hand, the thermoneutral voltage (1.15 V) accounts for the total change in enthalpy needed, providing a more appropriate point of comparison for electrolysis at low temperatures (<100°C). This value assumes heat required to overcome reaction entropy is provided by Ohmic heating from the kinetic overpotential of the anodic and cathodic half-reactions. In comparison, the thermoneutral potential for water splitting is 1.48 V under standard conditions (Dotan et al., 2019).

The minimum energy requirements are an idealized and unrealistic case; in reality, the overpotential needed to access intermediates along the most energetically favored reaction pathway is typically >500 mV and in many cases >1 V (Zhang et al., 2019). The high cathodic overpotential needed, together with several other factors including anodic overpotential and cell series resistance, make the cell potential required to drive electrochemical CH₄ formation significantly higher than its thermoneutral potential (Torelli et al., 2016). There are corresponding photocatalytic and photoelectrochemical pathways, but they are less competitive than the direct electrochemical pathway due to lower stability and energy conversion efficiency when compared with combined photovoltaic-electrolyzer systems, practical challenges of collecting a combustible gaseous product over large surface areas, and other technical challenges similar to the production of solar hydrogen that have been described elsewhere (Ardo et al., 2018).

A more developed pathway for CH₄ production is hydrogenation of CO₂ using H₂ produced by water electrolysis. CO₂ methanation, or CO₂ hydrogenation to CH₄, is a mature technology having been developed in the early 1900s. It was the subject of the 2012 Nobel Prize that was given in part to Paul Sabatier for its discovery using nickel metal as a catalyst, following the reaction shown in Equation 3 (Senderens and Sabatier, 1902).

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165.0 \text{kJmol} 
\quad \text{(Equation 3)}
\]

In the following century, several new metal catalysts and production methods were identified for what became known as the Sabatier reaction, with evidence showing Ru as the most active catalyst (Renda et al., 2020; Duyar et al., 2015), followed by Ni (Guilera et al., 2019), Co (Shin et al., 2016), Fe (Franken and Heel, 2020), and Mo (Rönsch et al., 2016). Industrially, CO₂ methanation has been used to remove trace CO and CO₂ from H₂ feed streams in the Haber-Bosch process, although this application could also be achieved through the production of CH₃OH. Unique to the Sabatier reaction, however, are its rates and kinetic selectivity. CO₂ methanation proceeds with much higher selectivity (99.4% using a standard Ni catalyst on an Al₂O₃ support) than the corresponding hydrogenation reaction using CO (62.2% using the same catalyst), making routes from CO₂ less competitive for CH₄ production (Fujita and Takezawa, 1997).

Both the thermocatalytic Sabatier process and the electrocatalytic process face challenges that ultimately affect their techno economics and viability for deployment. The most mission-critical challenges for deployment in space and on Mars are safety, robustness, and stability, which are yet unproven for CO₂ electrolysis of CH₄ at relevant scales. The Sabatier system combined with water electrolysis, on the other hand, has demonstrated sufficient performance durability, resilience to mechanical vibration, and ease of maintenance to enable its current use on the International Space Station for water recycling (Vogt et al., 2019). Going forward, as more robust and efficient CO₂ electrolysis systems are engineered, their lower operational temperatures and pressures provide an opportunity to decrease system weight as compared with
the Sabatier system. This potentially substantial reduction in payload mass could compensate for their lower productivity if current densities reach 1.0 A/cm²; the current state-of-the-art is around 100 mA/cm² (Rasouli et al., 2020). Figure 1 shows an energy diagram to further compare the two and assess where major energy losses occur, which highlights the significant loss from cathode overpotential.

DEPLOYMENT ON EARTH AND IN SPACE

It is clear from over 45 pilot, demonstration, and commercial scale power-to-gas deployments that CO₂ methanation combined with H₂O electrolysis is at a later stage of development and a more practical technology at present (Bailera et al., 2017). Several CO₂ methanation pilot plants have been deployed since the late 1990s, and in 2013 the first 6.3 MW wind-powered commercial plant that can produce 1,000 tonnes CH₄ per year was deployed by Audi in Werlte, Germany to demonstrate production of transportation fuels for Audi’s fleet of compressed natural gas (CNG) vehicles (Otten, 2014). For this facility and several others since, the cost of electricity and H₂ dictates plant economics, which makes variable operation following grid renewable energy supply critical (Thema et al., 2019).

In 2019, Air Company and the Charles Stark Draper Laboratory designed and built a flexible fuel production prototype system deployed in Cambridge, Massachusetts (Figure 2). The system is capable of producing CH₄, as well as liquid fuels CH₃OH and CH₃CH₂OH depending on the catalyst loaded into the flow reactor, from CO₂, H₂O, and electricity. The system uses a 4.5 kW NEL Series S20 electrolyzer for H₂ production, a fixed bed hydrogenation reactor, and heterogeneous catalysts produced by Air Company. The scale of the system was targeted to showcase a compact design that could produce liters of fuel at a time compared with common lab-based systems that produce on the milliliter scale. This enabled exploration of system-level efficiencies and improved technology at production levels relevant for further scale-up.

Although the economics of CO₂ methanation on Earth still favor natural gas despite the climatic risk of unmitigated drilling and consumption, there are additional value propositions for CO₂ methanation in space. CH₄ provides optimal recycling of atomic oxygen from CO₂ by producing H₂O, which enabled its deployment on the ISS in 2010 (Samplatsky et al., 2011). Although the CH₄ is currently vented, the system generates cost savings by reducing the need to launch over 900 kg of water to space under optimal operation. Development of the ISS Sabatier reactor highlighted some of the unique challenges to deploying CO₂ conversion systems in space. The gas-liquid separator, which is typically gravity-fed on Earth, is also redesigned as a rotary pump separation system. The ruthenium catalyst and alumina scaffold requirements include both performance and mechanical durability to survive high vibration loads during launch (Junaedj et al., 2011). Improved reactor and catalyst design together with the future potential for lightweight CO₂ electrolysis systems inform system-level optimization and further utilization of produced CH₄ for mass conservation.
As the space industry continues to grow in the future, for Lunar and Mars missions as well as rapid transit on Earth, design of rocket engines has focused on reusability as a critical cost factor. Despite the currently in-development SpaceX Starship having a higher capacity than existing vehicles, its marginal cost per launch is the lowest of any in development due to full reusability (Musk, 2018). This has prompted extensive development on rockets that use liquid methane and liquid oxygen as propellant, rather than kerosene and liquid oxygen or hydrogen and liquid oxygen. Liquid methane burns at a higher temperature and cleaner than kerosene and is more stable without embrittling metals as hydrogen does, lending to rocket reusability.

CH₄ can also be produced in situ on Mars from its atmosphere that contains >95% CO₂ (Franco et al., 2019). The Martian atmosphere is low pressure (0.1 psi) and contains Ar, N₂, and O₂ gases; therefore, a CO₂ electrolysis or methanation system with a catalyst that is tolerant of Ar, N₂, and O₂ would be desirable (Muscatello and Santiago-Maldonado, 2012). Because the product CH₄ would have to be liquefied, there is also potential to electrochemically reduce the required number of compression stages and simplify the overall system. This is in practice with H₂O electrolyzers, and although possible in theory with a pressure differential across a zero-gap CO₂ electrolyzer, it has not yet been demonstrated.

To launch a heavy vehicle such as the Starship from Earth, 240 tonnes of CH₄ and 860 tonnes of O₂ are needed (Musk, 2018). A propellant production system that uses only air, H₂O, and renewable electricity to meet these needs within a two-week time frame is proposed in Figure 3. Construction of an Earth-based or propellant depot would prove the concept of production from CO₂ at scale and serve to act as a renewable fuel for continued spaceflight by drawing the carbon required for launch from the air, rather than from the ground, for a closed carbon loop. This propellant depot could be based on Earth and bring liquid O₂ and CH₄ into space for orbital refueling or is lightweight enough to sit in orbit so that less reactive H₂O and liquefied CO₂ can be transported and liquid O₂ and CH₄ produced in orbit using photovoltaic-harvested energy from the sun unobstructed by Earth’s atmosphere.

For deployment on Mars, the bolded lines in Figure 3 delineate subsystem boundaries for optimal construction on Earth, thermal integration, and interplanetary transportation. These system boundaries remain valid for systems with output as small as 0.5 tons CH₄ per day. Because the gravitational acceleration on Mars is 38% of Earth’s, only around 7% of the lift-off propellant load is needed for a return trip, resulting...
in smaller system requirements for Martian refueling stations (Musk 2017). As liquefied CO$_2$ and H$_2$O are easier to store and less hazardous and explosive than CH$_4$ and O$_2$, a design such as this would enable safer orbital refueling stations.

In either Martian or orbital cases, the reactor would need to be transported significant distances, and Table 1 shows that total payload weight and volume would account for approximately 50 tonnes and 372 m$^3$, respectively, based on mass and volume of a currently operating CO$_2$ hydrogenation system. This is one-third of a Starship’s projected 150-tonne payload capacity, using equipment that is not optimized for space travel (Musk 2018). The Current Values shown in Table 1 reflect these numbers; however, they are the worst-case scenario because they reflect systems built without regard for weight and volume, for example, using carbon steel for structural elements rather than more lightweight titanium alloys. In a scenario where a propellant depot is being established on Mars, it is much more likely the production system would be optimized for spaceflight by using lightweight metals and composite materials, more efficiently utilizing the internal volume of the systems and improved state-of-the-art with respect to electrolyzer efficiency, which are reflected in the Optimized column in Table 1.

**Figure 3.** Block flow diagram for a proposed system to produce liquid methane and oxygen from CO$_2$ and H$_2$O that would take approximately 300 h to fully refuel a Starship

The system minimizes the need for moving mechanical components and is comprised of two subsystems that can be containerized for compact transportation.

Table 1. Material sizing and estimated component masses for a 19 ton/day cryo-methane production system using today’s materials based on size and weight of a comparably sized Air Company CO$_2$-to-alcohols system, alongside parameters for a mass-optimized future scenario

| Parameter                        | Current value | Optimized |
|----------------------------------|---------------|-----------|
| Subsystem 1 weight (kg)          | 35,000        | 11,000    |
| Subsystem 1 volume (m$^3$)       | 280           | 190       |
| Electrolyzer energy consumption (MWh/day) | 428           | 342       |
| Subsystem 2 weight (kg)          | 14,500        | 9,000     |
| Subsystem 2 volume (m$^3$)       | 92            | 60        |
| CO$_2$ to methane reactor weight (kg) | 2,000         | 500       |
| Subsystem 2 energy consumption (MWh/day) | 46            | 12        |
Once a CO₂ methanation system reaches Mars, there are use cases where the two subsystems are operated from their respective containers; however, there may be advantages to unpacking these containers and anchoring individual components on the Martian surface. Depending on the pressures required by the Sabatier reactor, storage tanks could be compacted for transport and inflated on the Martian surface, reducing the required transport volume. Because >90% of harvested electricity is used by the H₂O electrolyzer, power control systems may be situated in a single container that houses the electrolyzer, system communications, and O₂ liquefaction, all physically separated from H₂ storage. A diagram showing one potential layout of these components on the Martian surface is shown in Figure 4.

CONCLUSION
To advance electrochemical CO₂ conversion for applications on Earth and in space, use cases that best take advantage of relative strengths and mitigate weaknesses of CO₂ utilization technologies are needed. A frequent challenge faced by electrosynthesis technologies on Earth is the high cost of capital required upfront for system deployment. Applications in space mitigate this disadvantage because cost is not nearly as critical as the function CO₂ utilization offers, such as life support. Further research to improve system robustness, safety, and flight readiness can expand these uses to include in situ resource utilization on Mars. Removing and using CO₂ in space stations and on Mars helps to enable human expansion beyond Earth, as CO₂ methanation has already proven to be an effective chemical recycling tool in space.

The next step for development of CO₂ methanation for aerospace is terrestrial rocket propellant production and use to prove this concept. Several feasibility studies and experiments on prototype scales are underway. Refueling systems on Earth can decrease the carbon impact of launches into space, demonstrate fueling a rocket engine using the output gas from a Sabatier reactor, and enable research on process integration for optimal orbital or Martian propellant conditions. Furthermore, the deployment of propellant depots for other planets and satellites, where liquid methane and oxygen produced on Earth or Mars can be transported and stored, establishes interplanetary refueling stations that increase the distance that humanity can feasibly reach within our solar system.

ACKNOWLEDGMENTS
The author acknowledges NASA Centennial Challenges for a Phase I award from the CO₂ Conversion Challenge. The author thanks Air Company and the Charles Stark Draper Laboratory for their partnership deploying the demonstrator system for continuous fuel production, in particular Gregory Constantine, Jackson Constantine, Morgan Sparkes, Jodi Taylor, Dr. Chi Chen, Santiago Gonzalez Hernandez, Nicholas Steinke, Christopher Tuozzolo, Dr. Peter Miraglia, Christopher Williams, and James Cousens, as well as Rajlaxmi Jain for assistance illustrating Figure 4.
DECLARATION OF INTERESTS

The author has submitted patents on carbon dioxide conversion technologies. The author is an employee and shareholder of Air Company, which has a financial interest in these patents.

REFERENCES

Ardo, S., Rivas, D.F., Modestino, M.A., Greving, V.S., Abdi, F.F., Lladó, E.A., Artero, V., Ayers, K., Battaglia, C., Becker, J.P., et al. (2018). Pathways to electrochemical solar-hydrogen technologies. Energy Environ. Sci. 11, 2768–2763.

Bailer, M., Lisbona, P., Romeo, L.M., and Espatolero, S. (2017). Power to Gas projects review: lab, pilot and demo plants for storing renewable energy and CO2. Renew. Sustain. Energy Rev. 69, 292–312.

Barnes, J.J., McCubbin, F.M., Santos, A.R., Day, J.M.D., Boyce, J.W., Schwenzer, S.P., Ott, U., Franchi, I.A., Messenger, S., Anand, M., and Agee, C.B. (2020). Multiple early-formed water reservoirs in the interior of Mars. Nat. Geosci. 13, 264–264.

Blanco, D.E., and Modestino, M.A. (2019). Organic electrosynthesis for sustainable chemical manufacturing. Trends Chem. 1, 8–10.

Chen, K., Khosrowabadi Kotyk, J.F., and Sheehan, S.W. (2018). Progress toward commercial application of electrochemical carbon dioxide reduction. Chem 4, 2571–2586.

Desp, P., Rovira-Alsina, L., Sanchez, C., Dinesh, G.K.T., Tong, W., Chatterjee, P., Tedesco, M., Farras, P., Hamelers, H.M.V., and Puig, S. (2021). Microbial electrolysinae toward sustainable biorefineries for production of green chemicals from CO2 emissions. Biotechnol. Adv. 46, 107675.

Dotan, H., Landman, A., Sheehan, S.W., Malviya, K.D., Shter, G.E., Grave, D.A., Arzi, Z., Yehuda!, N., Halabi, M., Gal, N., et al. (2019). Decoupled carbon dioxide reduction with organic oxidation. Nat. Energy 4, 786–795.

Duyar, M.S., Ramachandran, A., Wang, C., and Farrauto, R.J. (2015). Kinetics of CO2 methanation over RuO2–Al2O3 and implications for renewable energy storage applications. J. Co2 Util. 12, 27–33.

Franco, C., Devor, R.W., Snyder, S.J., Petersen, E., and Hintre, P.E. (2019). Study of Sabatier Catalyst Performance for a Mars ISRU Propellant Production Plant. 49th International Conference on Environmental Systems, 7-11 July 2019, Boston, Massachusetts.

Franken, T., and Heel, A. (2020). Are Fe based catalysts an upcoming alternative to Ni in CO2 methanation at elevated pressure? J. Co2 Util. 39, 101175.

Fujita, S.I., and Takezawa, N. (1997). Difference in the selectivity of CO and CO2 methanation reactions. Chem. Eng. J. 68, 63–68.

Gonzalez Hernandez, S., and Sheehan, S.W. (2020). Comparison of carbon sequestration efficacy between artificial photosynthetic carbon dioxide conversion and timberland reforestation. MRS Energy Sustain. 7, E32.

Guilera, J., del Valle, J., Alarcon, S., Diaz, J.A., and Andreu, T. (2019). Metal-oxide promoted Ni/Al2O3 as CO2 methanation micro-size catalysts. J. Co2 Util. 30, 11–17.

Haynes, W.M. (2014). CRC Handbook of Chemistry and Physics (CRC Press).

Hoegh-Guldberg, O., Jacob, D., Taylor, M., Guillen Bolanos, T., Bindl, M., Brown, S., Camilloni, J.A., Diedhiou, A., Djaltane, R., Ebi, K., et al. (2019). The human imperative of stabilizing global climate change at 1.5°C. Science 365, eaaw9674.

Jacobsen, T.A., Kjer, J.S., Hemke, M.T., Braun, R.K., Meyer, K.C., and Funk, W.E. (2011). Direct human health risks of increased atmospheric carbon dioxide. Nat. Sustain. 2, 691–701.

Junaudi, C., Hawley, K., Walsh, D., Roychoudhury, S., Abney, M.B., and Perry, J.L. (2011). Compact and Lightweight Sabatier Reactor for Carbon Dioxide Reduction. 41st International Conference on Environmental Systems, 17 - 21 July 2011, Portland, Oregon.

Katelhon, A., Meys, R., Deutz, S., Suh, S., and Bardow, A. (2019). Climate change mitigation potential of carbonate capture and utilization in the chemical industry. Proc. Natl. Acad. Sci. USA 116, 11187–11194.

Lüthi, D., Le Floch, M., Berreiter, B., Bluner, T., Bnmola, J.M., Siegenthaler, U., Raynaud, D., Jouzel, J., Fischer, H., Kawamura, K., and Stocker, T.F. (2008). High-resolution carbon dioxide concentration record 650,000–800,000 years before present. Nature 453, 379–382.

Mitchell, C. (2016). Momentum is increasing towards a flexible electricity system based on renewables. Nat Energy 1, 15030.

Muscatello, A. and Santiago-Maldonado, E. (2012). Mars In Situ Resource Utilization Technology Evaluation. 50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, 9 - 12 January 2012, Nashville, Tennessee.

Musch, E. (2018). Making life multi-planetary. New Space 6, 2–11.

Musch, E. (2017). Making humans a multi-planetary species. New Space 5, 46–61.

Na, J., Seo, B., Kim, J., Lee, C.W., Lee, H., Hwang, Y.J., Min, B.K., Lee, D.K., Oh, H.S., and Lee, U. (2019). General technoeconomic analysis for electrochemical coproduction coupling carbon dioxide reduction with organic oxidation. Nat. Commun. 10, 5193.

Nangombe, S., Zhou, T., Zhang, W., Wu, B., Hu, S., Zou, L., and Li, D. (2018). Record-breaking climate extremes in Africa under stabilized 1.5 °C and 2 °C global warming scenarios. Nat. Clim. Change 8, 375–380.

Orella, M.J., Brown, S.M., Leonard, M.E., Roman-Leshkov, Y., and Brushtett, F.R. (2020). A general technoeconomic model for evaluating emerging electrolytic processes. Energy Technol. 8, 1900994.

Otten, R. (2014). The First Industrial PtG Plant – Audi E-Gas as Driver for the Energy Turnaround. CEDEC Gas Day 2014. http://www.cedec.com/files/default/8-2014-05-27-cedec-gas-day-reinhard-otten-audi-ag.pdf.

Peters, R., Balruevet, M., Grube, T., Samsun, R.C., and Stolten, D. (2019). A techno-economic analysis of the power to gas route. J. Co2 Util. 34, 616–634.

Prieto, G. (2017). Carbon dioxide hydrogenation into higher hydrocarbons and oxygenates: thermodynamic and kinetic bounds and progress with heterogeneous and homogeneous catalysis. ChemSusChem 10, 1056–1070.

Rasouli, A.S., Wang, X., Wicks, J., Lee, G., Peng, T., Li, F., McCammon, C., Dinh, C.T., Ip, A., Sinton, D., and Sargent, E.H. (2020). CO2 electroreduction to methane at production rates exceeding 100 mmol/m2. ACS Sustain. Chem. Eng. 8, 14668–14673.

Renda, S., Ricca, A., and Palma, V. (2020). Precursor salts influence in Ruthenium catalysts for CO2 hydrogenation to methane. Appl. Energy 279, 115767.

Ronsch, S., Schneider, J., Matthiexche, S., Schluter, M., Gotz, M., Lefebvre, J., Prabhakaran, P., and Bajohr, S. (2016). Review on methanation – from fundamentals to current projects. Fuel 166, 276–296.

Samplatsky, D.J., Grohs, K., Edeen, M., Crusan, J., and Burke, R. (2011). Development and Integration of the Flight Sabatier Assembly on the ISS. 41st International Conference on Environmental Systems, 17 - 21 July 2011, Portland, Oregon.

Sarp, S., Gonzalez Hernandez, S., Chen, C., and Sheehan, S.W. (2021). Alcohol production from CO2 hydrogenation to methane. Appl. Energy 279, 115767.

Shin, H.H., Lu, L., Yang, Z., Kiely, C.J., and McIntosh, S. (2016). Cobalt catalysts decorated with platinum atoms supported on barium zirconate provide enhanced activity and selectivity for CO2 methanation. ACS Catal. 6, 2811–2818.
Smith, W.A., Burdyny, T., Vermaas, D.T., and Geerlings, H. (2019). Pathways to industrial-scale fuel out of thin air from CO₂ electrolysis. Joule 3, 1822–1834.

Spurgeon, J.M., and Kumar, B. (2018). A comparative technoeconomic analysis of pathways for commercial electrochemical CO₂ reduction to liquid products. Energy Environ. Sci. 11, 1536–1551.

Thema, M., Bauer, F., and Sterner, M. (2019). Power-to-Gas: electrolysis and methanation status review. Renew. Sustain. Energy Rev. 112, 775–787.

Torelli, D., Francis, S.A., Crompton, J.C., Javier, A., Thompson, J.R., Brunschwig, B.S., Sonaga, M.P., and Lewis, N.S. (2016). Nickel–Gallium-catalyzed electrochemical reduction of CO₂ to highly reduced products at low overpotentials. ACS Catal. 6, 2100–2104.

Trisos, C.H., Merow, C., and Pigot, A.L. (2020). The projected timing of abrupt ecological disruption from climate change. Nature 580, 496–501.

U.S. Energy Information Administration (2020). United States Natural Gas Industrial Price. https://www.eia.gov/dnav/ng/hist/n3035us3m.htm.

Vogt, C., Monai, M., Kramer, G.J., and Weckhuysen, B.M. (2019). The renaissance of the Sabatier reaction and its applications on Earth and in space. Nat. Catal. 2, 188–197.

Wang, Y., He, D., Chen, H., and Wang, D. (2019). Catalysts in electro-, photo- and photoelectrocatalytic CO₂ reduction reactions. J. Photochem. Photobiol. C. 40, 117–149.

Warren, R., Price, J., Graham, E., Forstenhaeusler, N., and VanDerWal, J. (2018). The projected effect on insects, vertebrates, and plants of limiting global warming to 1.5°C rather than 2°C. Science 360, 791–795.

Zhang, H., Chang, X., Chen, J.G., Goddard, W.A., Xu, B., Cheng, M.J., and Lu, Q. (2019). Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane. Nat. Commun. 10, 3340.

Zimmerman, J.B., Anastas, P.T., Erythropel, H.C., and Leitner, W. (2020). Designing for a green chemistry future. Science 367, 397–400.

Zimmermann, A.W., and Schomacker, R. (2017). Assessing early-stage CO₂ utilization technologies—comparing apples and oranges? Energy Technol. 5, 850–860.