Sustainable Energy & Fuels

Radiation-assisted electrochemical reduction of CO2 to CO

Journal:	*Sustainable Energy & Fuels*
Manuscript ID	SE-COM-04-2024-000484.R1
Article Type:	Communication
Date Submitted by the Author:	13-Nov-2024
Complete List of Authors:	Morco, Ryan; Idaho National Laboratory, Diaz, Luis; Idaho National Laboratory, Biological and Chemical Processing Ramirez Corredores, Maria Magdalena; Idaho National Laboratory,

Radiation-assisted electrochemical reduction of CO_2 to CO

Ryan P. Morco, Luis A. Diaz and Maria Magdalena Ramirez-Corredores⁎

Energy and Environment Science and Technology, Idaho National Laboratory, Idaho Falls, ID, United States

Corresponding Author

⁎Maria Magdalena Ramirez-Corredores. ⁎ mariamagdalena.ramirezcorredores@inl.gov

Abstract

Carbon monoxide (CO) is a versatile intermediate feedstock for many applications, which can be produced from the electrochemical reduction of carbon dioxide (CO_2). However, current electrochemical CO production is associated with high overall costs due to low conversion efficiencies and high energy requirements. Here we report a unique way of enhancing the electrochemical reduction of CO_2 to CO using gamma (γ) photons. γ-Irradiation of the electrochemical cell setup induces the production of $e^{\bullet-}$ that results in an increase in CO_2 ionization as well as production of excited CO_2 (CO_2*) molecule with lower energy barrier. The ionized ($CO_2^{\bullet-}$) is quickly stabilized over a silver catalyst providing an alternative low activation energy route for CO_2 reduction. A decrease on the overpotential barrier enhanced the electrochemical reduction of CO_2 to CO by 25%.

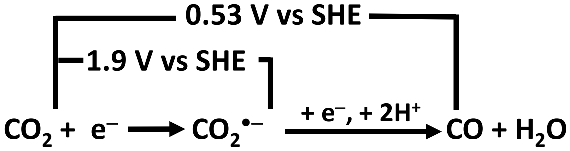
Introduction

Increase in carbon dioxide (CO_2) emissions and accumulation in the atmosphere is driven by the growing in population that heavily relied on fossil fuel power sources.[1] One of the grand challenges facing the world today is to prevent the damaging impact of climate change by urgently reducing the CO_2 emissions. One of the defined strategies is the development and implementation of carbon capturing and utilization (CCU) technologies.[2, 3] Over the last decade, there have been numerous technological developments on CO_2 capture and sequestration, as well as in the development of solutions to transform CO_2 into valuable products. The chemical conversion of CO_2 is a high energy demanding process. Carbon dioxide is one of the most stable molecules with low reactivity associated to its very low standard gibs free energy of formation ΔG° (−396 kJ·mol−1) and high activation energy barriers for its reactions.[4] One of the common methods to convert CO_2 is by the process called dry reforming of methane where CO_2 and methane (CH_4) are reacted at high temperature (>600 °C) to generate carbon monoxide (CO) and hydrogen gas (H_2), a mixture known as the synthetic gas (syngas).[5] Another method gaining popularity is by the direct electrochemical reduction of CO_2 (ECRCO2) to valuable products.[6] This method is particularly appealing because it can leverage the connection of carbon-free electrical energy to manufacture chemicals, materials and products and reduce the dependency on fossil sources.[7]

While the ECRCO2 presents a promising avenue for addressing climate change and provides sustainable resources for important chemical production,[7] multiple factors, such as low energy efficiency, low product selectivity, and poor process stability have hindered the deployment of this technology.[8] Over the years, numerous studies have been conducted to achieve efficient CO_2 reduction by electrochemical methods, aiming to convert CO_2 into commodities or valuable intermediates. Most studies in this field have focused on improving catalytic properties to enhance the efficiency of electrochemical reduction. Electrocatalysts are central in providing an alternative pathway with lower activation energy. In the search for improvements on both reaction rate and selectivity, researchers have explored various catalyst materials and designs, [6, 9-17] catalysts sizes and orientations, [9-12] as well as using cheaper non noble metal alternatives.[13-17]

Significant advancements have also been made in the engineering of functional electrodes, particularly in the application of gas diffusion electrodes (GDE)[18-21] as well as in the membrane electrode assembly (MEA)[22-24] and in understanding the effects of flow distributions, all of which are relevant to improve the performance of CO_2 electrolysis.[25] While these studies have reported significant progress on product selectivity, yield, and stability, the energy efficiency of the ECRCO2 remains a challenge to achieve cost-competitive deployment.[26] To overcome the activation energy barriers, the stable nature of the CO_2 molecule requires application of high overpotentials.

In the ECRCO2 to CO, a key and versatile intermediate in the synthesis of a variety of chemicals and hydrocarbons[27], one of the suggested reaction mechanism proceeds through the formation of the intermediate anion radical $CO_2^{\bullet -}$.[28] The measured standard reduction potential for this radical has been reported as -1.9 V vs SHE[29], almost 1.4 V above the standard reduction potential for CO formation (Equation 1). Therefore, the formation of this intermediate might be responsible for the high ECRCO2 overpotential.[30]



(1)

Nevertheless, it is important to emphasize that this intermediate radical was proposed to be formed on non-catalytic surfaces and additionally, on catalytic surfaces several other intermediates have been proposed to be formed through some other proposed mechanisms.[31-34] The performance capabilities of an electrocatalyst for changing the reaction mechanism and decreasing the activation energy lead to modifications in the exhibited potential. Thus, Au and Ag active catalytic phases have been reported to perform with the highest activity and to exhibit the lowest potential of -0.25V or -0.40V vs SHE, respectively.[31] These lower potentials are typically observed at very low values of current density, e.g. 2mA/cm^2 or 0.1mA/cm^2, respectively. The observed potential jumps considerably, at higher current densities, e.g., -0.7V[35] or -0.8V[36] for Ag catalysts, at respectively, 200mA/cm^2 or 350mA/cm^2.

In this work, we explored a new approach to overcome the CO_2 activation barrier of its electrochemical reduction to CO, by using ionizing radiation. The application of ionizing radiation in enhancing chemical processes is not a new concept. In fact, ionizing radiation can provoke excitation, ionization, neutralization, activation and chemical reactions, at low temperatures, on stable molecules, such as CO_2. Additionally, besides nuclear energy being a reliable, continuous and low-carbon resource, nuclear power plants (NPPs) can offer an unique feature of providing energy (otherwise wasted), in the form of ionizing radiation, electricity and heat, from the excess energy generated. There have been studies where ionizing radiation has been proposed to accelerate degradation processes in materials such as in an Advanced Oxidation Process (AOP) for water purification[37] or in improving materials properties such as in radiation-induced polymerization[38] and radiation-assisted nanoparticle synthesis.[39, 40] In particular the CO_2 reactions induced by radiation have been recently reviewed.[41] The demonstration that γ-radiation could induce the dry reforming reaction at room temperature[42], as well as the reduction to methanol (CH_3OH) assisted by high energy radiation[14] have been also reported. However, to the authors knowledge there is no report on radiation enhanced ECRCO2.

In this regard and considering the combined application of radiation to catalytic, electrochemical and/or electrocatalytic processes, the lifetime of the radiation-induced species have risen particular challenges.[43] The first challenge has been identified as whether to use ionizing radiation and the electrocatalytic process simultaneously or consecutively. Simultaneity appears to be the choice for instances when avoiding recombination reactions of ion-radicals needs to be pursued. In these cases, R&D might start by identifying whether there is any benefit or improving effect of the application of the radiation to the electrocatalytic process. However, most likely radiation will have also not only positive but negative effects on the multiple components of the system e.g., the electrocatalyst, the reacting molecules, the membrane and the electrolyte, which will open new opportunities for further research.

Experimental

The CO_2 electrolysis was performed using electrochemical cell hardware from Dioxide Materials. The setup as shown in Figure 1a consists of a 5 cm^2 two-compartment flow through cell, separated by a polymeric anion exchange membrane (Sustainion® X37-50 Grade RT membrane[23]). The cathode electrocatalyst was a silver coated porous carbon film while the anode was an IrO_2 coated carbon film, both of which are known for their respective selectivity for CO_2 to CO, and for the oxygen evolution reaction (OER). The cell was assembled by sandwiching the IrO_2 anode, anion exchange membrane and Ag-coated carbon cathode between an anode plate made of titanium and a stainless-steel cathode plate. Humidified CO_2 gas and liquid anolyte (10 mM $KHCO_3$) are fed to the cathode and anode, respectively, by means of mass flow controllers (Alicat Scientific). The 10mM $KHCO_3$ solutions is flowed at 3 $mL\cdot min^{-1}$ while the CO_2 flow at the cathode was 30 $mL\cdot min^{-1}$. These solutions were prepared using commercially obtained chemicals and high purity water and the total volume used was typically less than 1L.

The Electrolysis experiments were performed by supplying a potential of 3.2 V to the electrochemical cell from a potentiostat (Solartron SI-287). The electrolysis experiment was allowed a minimum of 6 hours stabilization, before collecting gas samples for analysis and exposing to γ-radiation. Potentiostatic measurements were initiated in the electrochemical cell first in the absence of γ-radiation until steady state was achieved with a baseline current of 900mA (~180 $mA\cdot cm^{-2}$). Irradiation experiments were carried at the INL Center for Radiation Chemistry using a Research Foss Therapy Services Model-812 Co-60 Self-Contained Irradiator (Figure 1b) where the electrochemical cell was exposed to a dose rate of ~180 $Gy\cdot min^{-1}$.

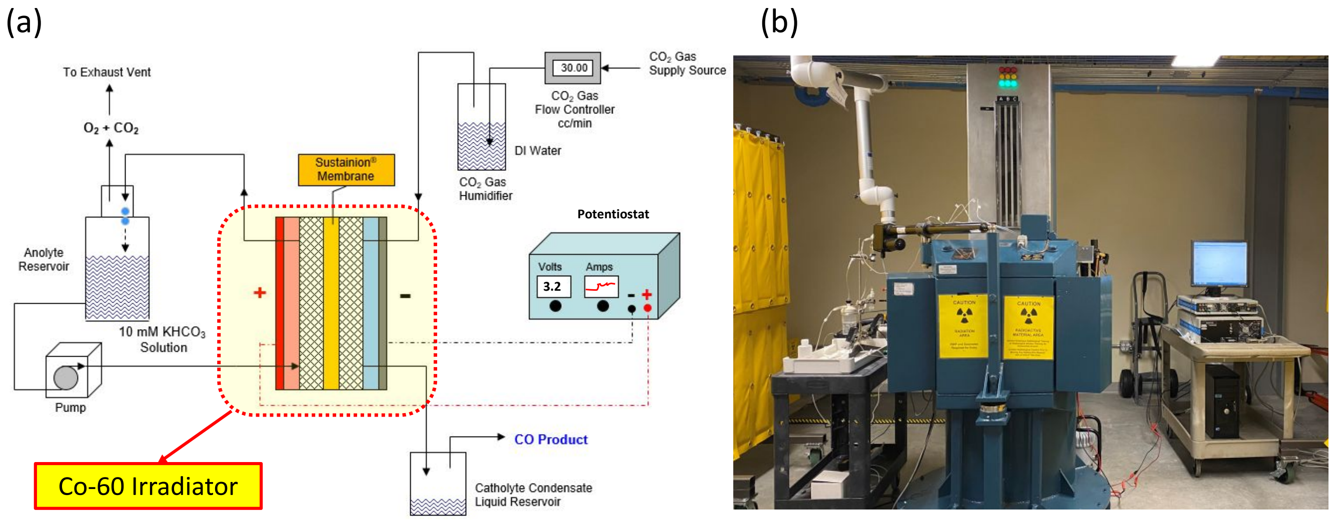


Figure 1. (a) Schematic of the radiation-assisted electrochemical reduction system; and (b) The Co-60 irradiator.

At this point, it would be worth describing some radiation related details. One of the most important parameters when evaluating radiation effects is the dose, which is a parameter used to measure the amount of radiation absorbed by an atom or molecule. The measuring unit is either the gray (Gy, SI unit, J/kg) or the rad (CGS unit, 100 erg/g, 0.01 Gy). In an irradiator, a radioactive element emit ionizing radiation at an intensity that decays over time and distance. Thus, the irradiation chamber does not have a uniform dose rate, which is the quantity of radiation absorbed or delivered per unit time. Based on the existing dosimetry (dose or dose rate calibration), there can be an order of magnitude variation of the dose rate within the irradiation chamber depending on sample position. Additionally, dosimetry has to be performed to correct any shielding from the sample cell. The dose rate at different sample positions within the irradiator has to be periodically calibrated and exposure time is estimated to administer the desired dose to a given sample. Since irradiator time and use are highly valuable, experiments have to be strictly planned and prepared, well in advance. These protocols and plans have to meet the most rigorous safety requirements.

The electrolysis gas products were collected in a Tedlar multilayer sampling bag (Restek) and the samples were analyzed by GC-TCD-BID. The volume of gas collected was measured using a gas syringe which is used to calculate the conversion efficiency of the experiment. Carbon dioxide conversion is calculated by the moles of CO in the gas product over the total moles of CO_2 in the gas product (CO and unreacted CO_2). Faradaic efficiency (FE) for CO and H_2 production were also calculated.

Results and Discussion

The most active and selective (to CO) catalyst for the ECRCO2 is Au, followed by Ag. In a typical room temperature (RT) experiment for the gas phase electrochemical reduction of CO_2, in the presence of water vapor or steam, using these highly active and selective electrocatalysts, the following gas products might be observed: CO, hydrogen, methane, and ethylene.[31] In a blank electrolysis experiment, run for a 1 hour the composition of the gas stream was estimated as 0.26g CO, 0.013g H_2 and 0.011g CH_4 (9.3, 6 and 0.7 mmol, respectively) and traces of ethylene, diluted by the unreacted CO_2. These results, showing CO and H_2 as the major products confirmed the high selectivity of the used Ag electrocatalyst, in the ECRCO2.

The current profile as a function of time, of the electrochemical experiment in the absence and in the presence of γ-irradiation can be seen in Figure 2.

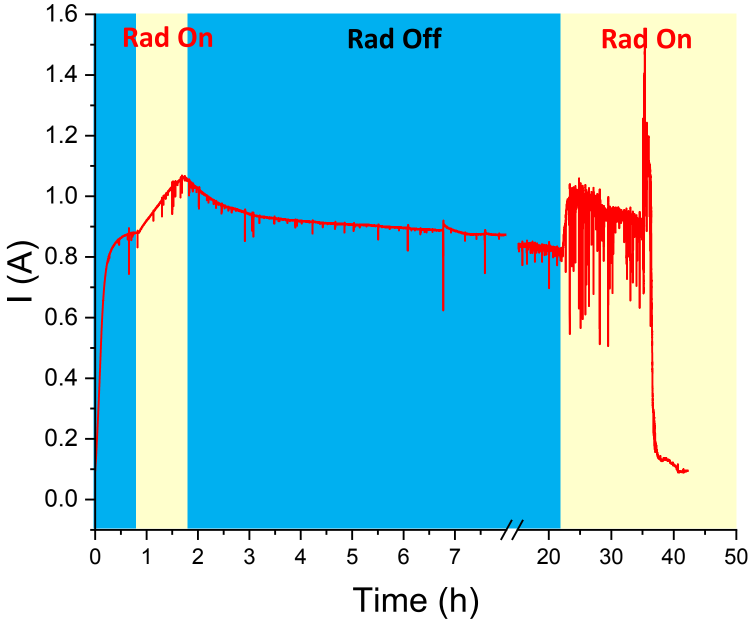


Figure 2. Current as a function of time under applied potential of 3.2 V in the absence and in the presence of γ-irradiation.

It can be observed (Figure 2) that immediately, upon γ-irradiation, the current increased from ~900 mA to nearly ~1,100 mA and as soon as the irradiation was stopped, the current dropped down to its baseline value. The irradiation was kept off overnight to verify the integrity of the cell components and its performance. Then, the electrochemical cell was subjected to irradiation again, reaching current values of 1,000mA and after about 20 h of irradiation, the current spiked to 1,600 mA but instantaneously dropped below 100 mA. Al this point, the EC cell had received a 36,000Gy dose and these results indicate that one (or more) component(s) could not tolerate such dose levels. These components need to be identified and the effects of ionizing radiation understood even though mitigating strategies including the search of radiation tolerant materials and components, as well as minimization of dose rate and the possibility of integrating two consecutive processes radiolysis followed by electrocatalysis, for instance would represent additional options.

Gas samples were collected at anode and cathode side throughout the experiment and the Faradaic efficiency (FE) for CO and H_2 as well as the operating current density at the points of sampling are presented in Figure 3.

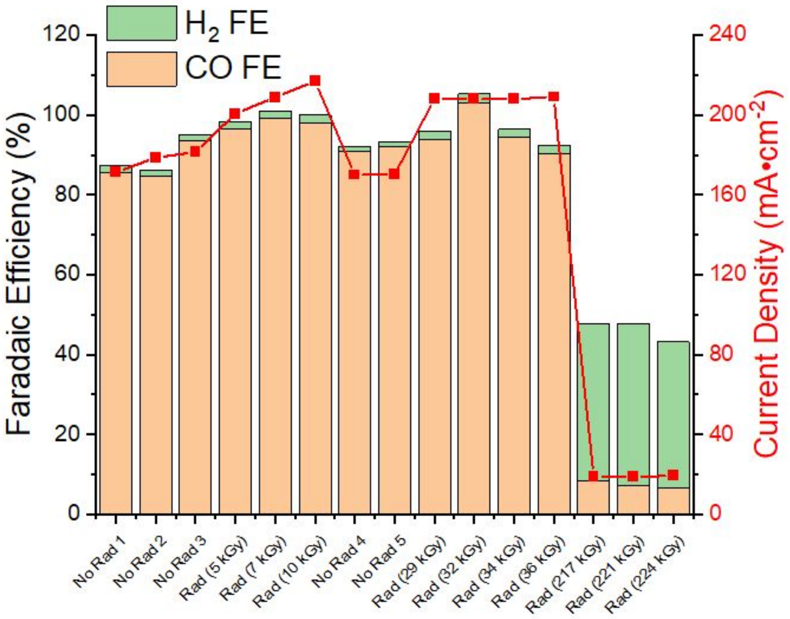


Figure 3. Faraday efficiency and electrochemical cell current density for CO and H_2 at 3.2 V applied potential in the absence and in the presence of γ-irradiation.

The comparison of the FE for CO and for H_2 demonstrates that γ-radiation affects conversion towards CO in a much greater extent than it does for H_2 production. This is somehow expected due to the larger size of the CO_2 molecule (larger cross section) than that of H_2O, providing a larger interaction area for the radiation to affect the CO_2 molecule. Additionally, it can also be noticed that FE does not add up to 100%, in most cases, and this is an indication of selectivity losses. At this point, it is worth noting that the screening of multiple catalytic phases (commonly carried out during the design and development of new electrocatalysts) is focused on the reaction of interest and determination of activity (e.g., overpotential reduction) and selectivity (e.g., FE). Since we could only analyze the gas product and it only contained CO, H_2 and the unreacted CO_2, our plan includes the definition and development of a safe protocol for collecting and analyzing the liquid product (if any). The lack of selectivity of radiation-induced processes is a typical consequence of reaction mechanisms with (ion and free) radical intermediates. The use of radiation to induce the formation of highly reactive radicals from unreactive/stable molecules, like CO_2, set the basis for enhancing the reactions of CO_2 and its conversion into value-added products through more energy efficient processes. For the purpose of this exploratory experimentation, collecting evidence on the possibility to enhance the CO_2 electrochemical conversion, by using ionizing radiation was the target. These results indicate that the selectivity required from any electrocatalyst needs to be improved when the electrochemical process would be enhanced with ionizing radiation.

The cell performance collapse, after the 20 h of irradiation showed through a significant current drop was also evidenced by a drop in the measured CO concentration. In fact, the amount of gas collected after the big current drop decreased significantly. This performance collapse suggests that radiation might have caused significant deterioration of one or more of the cell components. Certain materials used in the manufacture of components are sensitive to radiation. For instance, polytetrafluoroethylene (PTFE) coating used to promote hydrophobicity in the GDE cathode and other polymeric materials (e.g., membranes) are known to undergo radiation-induced degradation.[44-47] This deterioration may affect the hydrophobic characteristics that prevents cathode flooding, for instance. The loss of hydrophobicity may have affected the selectivity towards CO conversion, as can be observed in the preferential increase of the H_2 generation (Figure 3). The effect of the radiation dose on the hydrophobicity of the cathode electrocatalyst in contact with the anolyte was examined. In Figure 4, the wettability of the cathode as a function of received dose is presented. The contact angle of water droplet over the cathode surface and the droplet shape were affected by radiation exposure. In unirradiated electrode (Figure 4a), the water cohesion appears to be stronger than surface adhesion, which is maintained even after the electrode had received a dose of 59 kGy (Figure 4b), as can be deduced from the droplet shape that did not undergo any change compared to the unirradiated electrode. Obvious changes on the droplet shape can be noticed in Figures 4c (after 129 kGy dose) and 4d (after 277 kGy dose) that indicate a much stronger adhesion with dose, confirming the damage of the surface hydrophobic coating. However, it is also known that a lack of hydrophobicity cannot be hold responsible of lowering activity or of a total deactivation of the electrocatalyst, which led to the electrochemical performance collapse.[48-50] Instead, hydrophobicity has been accepted to be associated with modulating selectivity, as observed in the present work.[49, 50]

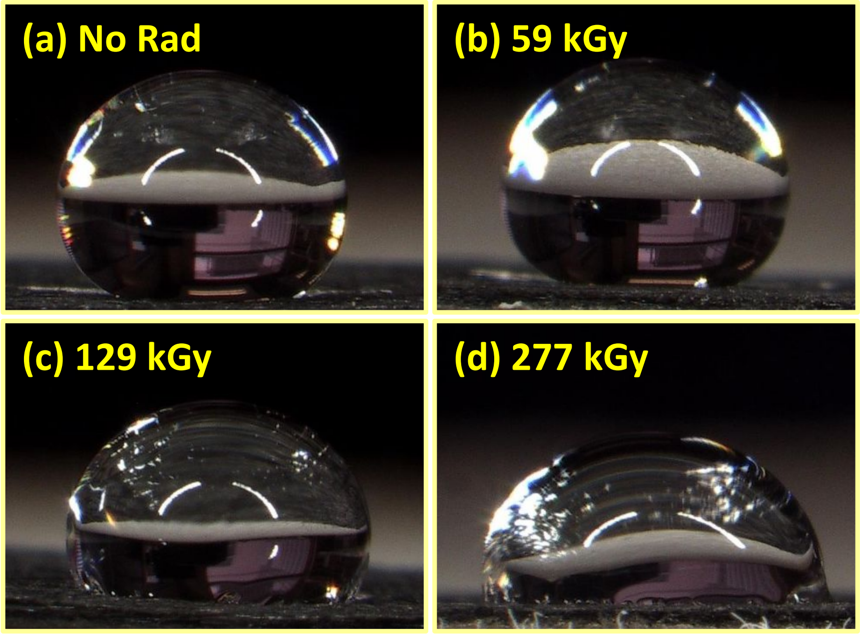


Figure 4. Water wettability of the cathode surface as a function of received dose.

The current decrease and the very low gas flow on the other hand suggest that there is an increase in internal ohmic resistance, which could be attributed to a decrease in electrolyte conductivity as a consequence of a damaged membrane. Regarding this potential membrane deterioration, this membrane was provided under a “non-analysis agreement” that precluded characterization studies. However, preliminary experiments were carried out to assess the radiation tolerance of the membrane, by testing and comparing the EC performance of an unirradiated membrane with that of another that was irradiated with a dose of 100 Gy (at 38.4 Gy/min). Although this commercially available membrane did not seem to show any mechanical effects, its conductivity was affected. Under that condition, the original current density of 200 mA cm^{-2} dropped to 50 mA cm^{-2}, upon irradiation. For this test, one could not ignore the deteriorating effect caused on the membrane by its shelf life. Thus, the observed deteriorated performance of the membrane, after its direct irradiation, could not be associated exclusively to irradiation and neither to its shelf life, due to a prolong time between membrane conditioning and the irradiation time. It might be also relevant, mentioning that the other components of the EC cell might exert a shielding/shadowing effect on radiation, which incentivize the assessment of performance under irradiation of the whole EC cell. It seems that the cell could perform quite well up to receiving 36,000 Gy of γ-ray dose, with the above mentioned benefits. Nonetheless, further studies on the radiation tolerance of different membranes are needed, together with a selection based on screening in terms of radiation tolerance first and then in EC performance.

While it is not clear the mechanism in which γ-radiation improved the CO_2 – CO conversion, there have been studies on the radiolytic reductive decomposition of CO_2 that report CO production, but the yield is poor and prolonged irradiation leads to back reactions lowering the yield further.[41-43] Those experiments are also performed under batch conditions unlike the flowing condition described in this paper.[42]

Typically, the proposed mechanism for ECRCO2 to CO involves the formation of $\bullet COOH_{ads}$, which can occur in a concerted single step (also known as proton coupled electron transfer, PCET) or in two separate steps, described below as reactions 2 and 3. For the two-steps mechanism, the initial step is the production of carbon dioxide radical anion ($CO_2^{\bullet-}$) that is then followed by accepting a proton (H^+). This adsorbed intermediate ($\bullet COOH_{ads}$) takes an electron (e^-) to decompose into CO and OH^- as shown in reaction 4.[51-55] Regarding Ag catalysts, both mechanisms might take place depending on the applied potential. It has been suggested that COOH* was the only reaction intermediate, within the potential range between −1.40 V and −1.55 V vs Ag/AgCl; while COO^-* was also observed, when the applied potential was −1.6 V vs Ag/AgCl.[55]

$$CO_2 + e^{\bullet-} \rightarrow CO_2{}^{\bullet-}{}_{ads} \tag{2}$$

$$CO_2{}^{\bullet-}{}_{ads} + H^+ \rightarrow \bullet COOH_{ads} \tag{3}$$

$$\bullet COOH_{ads} + e^{\bullet-} \rightarrow CO_{ads} + OH^- \tag{4}$$

Another alternative route involves the reaction of another CO_2 to the adsorbed $CO_2^{\bullet-}$ to form an oxalate radical.[51]

$$CO_2{}^{\bullet-}{}_{ads} + CO_2 \rightarrow [OCOCO_2]^{\bullet-}{}_{ads} \tag{5}$$

$$[OCOCO_2]^{\bullet-}{}_{ads} + e^{\bullet-} \rightarrow CO_{ads} + CO_3{}^{2-} \tag{6}$$

In the electrochemical reduction of CO_2, it is recognized that the initial reduction by e^- is the rate-determining step in which it happens as the CO_2 is adsorbed on the catalyst surface.[51] This slow step stems from the high activation of the inert CO_2 exhibited during structural rearrangement of CO_2 as it docks on the catalyst surface from linear to bent.[30, 56]

The observed improved CO_2-CO conversion seems to be the indirect effect of the γ-radiation, on CO_2 reduction. However, whether radiation is affecting the electrocatalyst, the activation or ionization of the CO_2 molecule and/or the interaction of electrocatalyst with the reacting molecules remain unknown to us. The redox active species possibly formed from the effect of the γ-radiation, on the water vapors carried from CO_2 humidifier were $H_2O•^+(g)$, $H_2(g)$, O(g), •OH(g), H(g), $•O^+(g)$, $e^{•-}$ (g), $H^+(g)$, $OH^+(g)$.

The generated species particularly e^- (g) might collide with CO_2 to form $CO_2^{•-}$ where it is readily adsorbed and stabilized on the Ag surface. Thus, γ-radiation provided an alternative route for producing $CO_2^{•-}$. This mechanism can be linked to the observed increase in current, underpinned by the decrease in one of the overpotential barriers of the reaction. Optionally, it could also be the result of the reduction in ohmic resistance or simply a decrease in the kinetic overpotential. At this point, one cannot clearly identify the exact contribution of each of these factors in the increase of the current. Regardless of the actual mechanism, the undeniable fact is that radiation enhances the electrochemical reduction of CO_2, probably by inducing ion-radicals formation.

$$CO_2 + e^{•-}(g) \rightarrow CO_2{}^{•-}{}_{ads} \quad (8)$$

The adsorbed ion-radical ($CO_2{}^{•-}{}_{ads}$) might then either go through the route of protonation or oxalate radical formation, prior to complete the CO formation. In our setup, a measurable amount of CO_2 was quantified over the anode side, which results from the possible CO_3^{2-} crossing the membrane indicates that the oxalate formation route might be the dominating pathway. The amount of CO_2 over the cathode is higher than in the anode in the absence of radiation. When γ-radiation was present, measured CO_2 in the anode increases more than the CO_2 in the cathode. The schematic depiction of this mechanism is illustrated in Figure 5. Generation of excited carbon dioxide (CO_2*) might be another contributing mechanism to explain the increase in the rate of CO_2 conversion. The ionization of excited states requires less energy compared to its ground state, thus lowering activation energy and leading to yield increase.

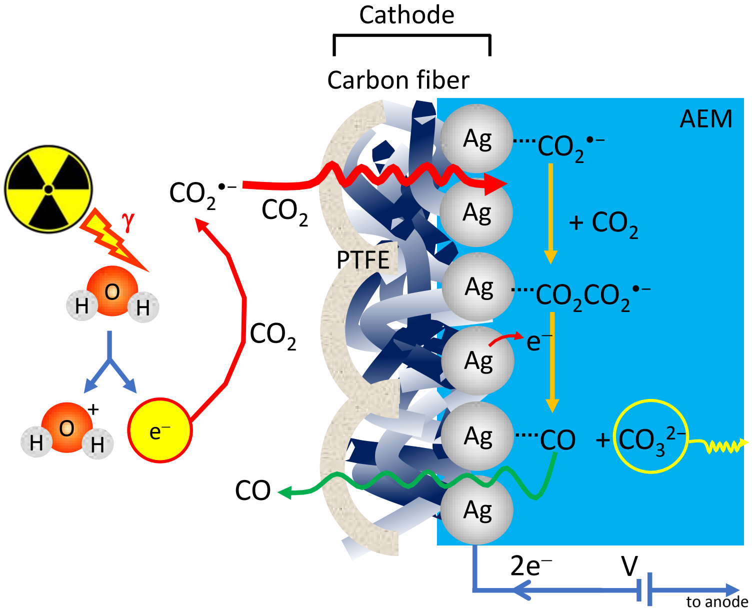


Figure 5. Schematic depiction of a suggested mechanism describing the radiation-assisted electrochemical CO_2 reduction.

In summary, evidently, γ-radiation improves CO_2 conversion to CO, as Figure 6 shows. As can be seen, in the absence of γ-radiation, the baseline conversion was about 20%, comparable to values reported in the literature.[57] Meanwhile, the conversion jumped to more than 25% by subjecting the cell to γ-radiation exposure. Thus, under γ-radiation a 5% increase in conversion represents a 25% performance improvement that translates into a corresponding increase in the CO yield. Clearly, radiation has exerted a positive effect on the electrocatalytic performance and could set the basis for the development of a new electrochemical process. As mentioned above, nuclear power plants can offer energy in the form of heat, electricity and radiation, the radiation-assisted electrochemical process postulated here could be the beginning of a research topic that would pursue the synergy between radiation and electricity though the opportunity also exist to improve the process, by increasing the operating temperature, using the third form of provided energy, heat.

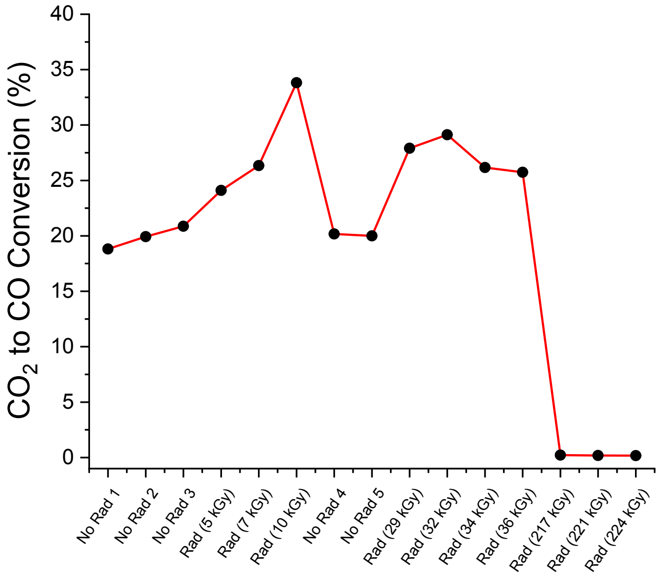


Figure 6. CO_2 to CO percent conversion as a function of received radiation dose.

Conclusions

Overall, we have demonstrated that ionizing radiation enhances the electrochemical reduction of CO_2 to CO. A 25% improvement of the CO_2-CO conversion is significantly enough to consider moving forward for future development, prioritizing the research to explore radiation tolerant electrochemical components. Regardless of which component was damaged by the radiation, it only collapsed after 36,000Gy dose. Therefore, it is important to determine the minimum dose rate that could enhance EC performance and more particularly the use of very low dose rates (e.g., a dose rate of 3Gy/min would prolong the operative period to 200h). Nevertheless, understanding the effects of radiation is also a priority and not only determining whether radiation affects the reaction mechanism, the electrocatalyst or the interaction between the reacting molecules and the electrocatalyst, it is also relevant to develop a detailed understanding of these interactions and effects.

Once the identified challenges are addressed and sorted out, the development and optimization of the proposed radiation-assisted ECRCO2 process not only involves the chemical process itself but also the efficient, safe, reliable, and cost-effective use of the radiation, power, and probably heat available in NPPs. This proposed (highly efficient)

ECRCO2 process represents an innovative integrated chemical-nuclear energy system that could facilitate the decarbonization of a hard to decarbonize chemical industry.

Author Contributions

Ryan P. Morco: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Resources, Data Curation Management, Writing - Original Draft, Writing - Review & Editing Preparation, Visualization Preparation. Luis A. Diaz: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Supervision, Writing - Review & Editing Preparation. Maria Magdalena Ramirez-Corredores: Conceptualization, Writing - Review & Editing Preparation, Supervision, Project Administration, and Funding Acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank the INL Center for Radiation Chemistry Research (CR2) for facilitating the conduct of irradiation experiment in this study. This research was funded by the Laboratory Directed Research & Development (LDRD) Program of Battelle Energy Alliance, LLC under DOE Idaho Operations Office contract No. DE-AC07-05ID14517.

References

1. H.-O. Pörtner, D. C. Roberts, M. Tignor, E. S. Poloczanska, K. Mintenbeck, A. Alegría, M. Craig, S. Langsdorf, S. Löschke, V. Möller, A. Okem and B. Rama, *Climate Change 2022: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II*, Report Sixth Assessment, Intergovernmental Panel on Climate Change (IPCC), Cambridge, UK., 2022.
2. P. C. Psarras, S. Comello, P. Bains, P. Charoensawadpong, S. Reichelstein and J. Wilcox, *Environmental Science and Technology*, 2017, **51**, 11440-11449.
3. P. Styring, E. A. Quadrelli and K. Armstrong, *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, Elsevier, Amsterdam, 2015.
4. M. Aresta, A. Dibenedetto, C. Pastore, I. Pápai and G. Schubert, *Topics in Catalysis*, 2006, **40**, 71-81.
5. M. S. Fan, A. Z. Abdullah and S. Bhatia, *ChemCatChem*, 2009, **1**, 192-208.
6. A. Kumar, L. M. Aeshala and T. Palai, *Journal of Applied Electrochemistry*, 2023, **53**, 1295-1319.
7. P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo and E. H. Sargent, *Science*, 2019, **364**, eaav3506.
8. S. Overa, B. H. Ko, Y. Zhao and F. Jiao, *Accounts of Chemical Research*, 2022, **55**, 638-648.
9. C. Kim, H. S. Jeon, T. Eom, M. S. Jee, H. Kim, C. M. Friend, B. K. Min and Y. J. Hwang, *Journal of the American Chemical Society*, 2015, **137**, 13844-13850.

10. A. Salehi-Khojin, H. R. M. Jhong, B. A. Rosen, W. Zhu, S. Ma, P. J. A. Kenis and R. I. Masel, *Journal of Physical Chemistry C*, 2013, **117**, 1627-1632.
11. D.-R. Yang, L. Liu, Q. Zhang, Y. Shi, Y. Zhou, C. Liu, F.-B. Wang and X.-H. Xia, *Science Bulletin*, 2020, **65**, 796-802.
12. Y.-C. Hsieh, S. D. Senanayake, Y. Zhang, W. Xu and D. E. Polyansky, *ACS Catalysis*, 2015, **5**, 5349-5356.
13. J. L. Dimeglio and J. Rosenthal, *Journal of the American Chemical Society*, 2013, **135**, 8798-8801.
14. C. Hu, Z. Jiang, Q. Wu, S. Cao, Q. Li, C. Chen, L. Yuan, Y. Wang, W. Yang, J. Yang, J. Peng, W. Shi, M. Zhai, M. Mostafavi and J. Ma, *Nature Communications*, 2023, **14**.
15. L. Peng, L. Shang, T. Zhang and G. I. N. Waterhouse, *Advanced Energy Materials*, 2020, **10**.
16. F. Quan, D. Zhong, H. Song, F. Jia and L. Zhang, *Journal of Materials Chemistry A*, 2015, **3**, 16409-16413.
17. J. Wu, S. Ma, J. Sun, J. I. Gold, C. Tiwary, B. Kim, L. Zhu, N. Chopra, I. N. Odeh, R. Vajtai, A. Z. Yu, R. Luo, J. Lou, G. Ding, P. J. A. Kenis and P. M. Ajayan, *Nature Communications*, 2016, **7**.
18. E. W. Lees, B. A. W. Mowbray, F. G. L. Parlane and C. P. Berlinguette, *Nature Reviews Materials*, 2022, **7**, 55-64.
19. T. Burdyny and W. A. Smith, *Energy & Environmental Science*, 2019, DOI: 10.1039/C8EE03134G.
20. T. N. Nguyen and C. T. Dinh, *Chemical Society Reviews*, 2020, **49**, 7488-7504.
21. K. L. Yang, R. Kas, W. A. Smith and T. Burdyny, *ACS Energy Letters*, 2021, **6**, 33-40.
22. J. Lee, J. Lim, C.-W. Roh, H. S. Whang and H. Lee, *Journal of CO2 Utilization*, 2019, **31**, 244-250.
23. R. B. Kutz, Q. Chen, H. Yang, S. D. Sajjad, Z. Liu and I. R. Masel, *Energy Technology*, 2017, **5**, 929-936.
24. R. I. Masel, Z. Liu and S. Sajjad, *ECS Transactions*, 2016, **75**, 1143-1146.
25. C. P. O'Brien, R. K. Miao, S. Liu, Y. Xu, G. Lee, A. Robb, J. E. Huang, K. Xie, K. Bertens, C. M. Gabardo, J. P. Edwards, C. T. Dinh, E. H. Sargent and D. Sinton, *ACS Energy Letters*, 2021, **6**, 2952-2959.
26. S. Jin, Z. Hao, K. Zhang, Z. Yan and J. Chen, *Angewandte Chemie International Edition*, 2021, **133**, 20795-20816.
27. X. Ma, J. Albertsma, D. Gabriels, R. Horst, S. Polat, C. Snoeks, F. Kapteijn, H. B. Eral, D. A. Vermaas, B. Mei, S. de Beer and M. A. van der Veen, *Chemical Society Reviews*, 2023, **52**, 3741-3777.
28. Y. Hori, H. Wakebe, T. Tsukamoto and O. Koga, *Electrochimica Acta*, 1994, **39**, 1833-1839.
29. H. A. Schwarz and R. W. Dodson, *The Journal of Physical Chemistry*, 2002, **93**, 409-414.
30. D. Sun, X. Xu, Y. Qin, S. P. Jiang and Z. Shao, *ChemSusChem*, 2020, **13**, 39-58.
31. X. Zhang, S.-X. Guo, K. A. Gandionco, A. M. Bond and J. Zhang, *Materials Today Advances*, 2020, **7**, 100074.
32. A. R. Woldu, Z. Huang, P. Zhao, L. Hu and D. Astruc, *Coordination Chemistry Reviews*, 2022, **454**, 214340.
33. W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang and Z. Jin, *Advanced Science*, 2018, **5**, 1700275.
34. J. Yu, J. Wang, Y. Ma, J. Zhou, Y. Wang, P. Lu, J. Yin, R. Ye, Z. Zhu and Z. Fan, *Advanced Functional Materials*, 2021, **31**, 2102151.
35. C.-T. Dinh, F. P. García de Arquer, D. Sinton and E. H. Sargent, *ACS Energy Letters*, 2018, **3**, 2835-2840.
36. S. Ma, R. Luo, J. I. Gold, A. Z. Yu, B. Kim and P. J. A. Kenis, *Journal of Materials Chemistry A*, 2016, **4**, 8573-8578.

37. M. Trojanowicz, A. Bojanowska-Czajka and A. Capodaglio, *Environmental Science and Pollution Research*, 2017, **24**, 20187-20208.
38. M. M. Ghobashy, in *Ionizing Radiation Effects and Application*, ed. B. Djezzar, InTech, Rijeka, Croatia, 2018, pp. 113-134.
39. T. I. Sutherland, C. J. Sparks, J. M. Joseph, Z. Wang, G. Whitaker, T. K. Sham and J. C. Wren, *Physical Chemistry Chemical Physics*, 2017, **19**, 695-708.
40. Y. Yang, M. Johansson, A. Wiorek, N. V. Tarakina, F. Sayed, R. Mathieu, M. Jonsson and I. L. Soroka, *Dalton Transactions*, 2021, **50**, 376-383.
41. M. M. Ramirez-Corredores, G. Gadikota, E. E. Huang and A. M. Gaffney, *Frontiers in Energy Research*, 2020, **8**, 17pp.
42. M. M. Ramirez-Corredores, H. W. Rollins, R. P. Morco, C. A. Zarzana and L. A. Diaz, *Journal of Cleaner Production*, 2023, **429**, #139539, 139513pp.
43. M. M. Ramirez-Corredores, L. A. Diaz, A. M. Gaffney and C. A. Zarzana, *Renewable and Sustainable Energy Reviews*, 2021, **150**, #111450, 111415pp.
44. S. R. Allayarov, S. V. Konovalikhin, Y. A. Olkhov, V. E. Jackson, L. D. Kispert, D. A. Dixon, D. Ila and U. Lappan, *Journal of Fluorine Chemistry*, 2007, **128**, 575-586.
45. P. G. Demertzis, R. Franz and F. Welle, *Packaging Technology and Science*, 1999, **12**, 119-130.
46. Y. Y. Astakhov, E. R. Klinshpont and V. K. Milinchuk, *Polymer Science U.S.S.R.*, 1988, **30**, 699-704.
47. Y. Y. Astakhov, E. R. Klinshpont and V. K. Milinchuk, *Polymer Science U.S.S.R.*, 1988, **30**, 2783-2790.
48. D. Hursán, A. A. Samu, L. Janovák, K. Artyushkova, T. Asset, P. Atanassov and C. Janáky, *Joule*, 2019, **3**, 1719-1733.
49. D. Wakerley, S. Lamaison, F. Ozanam, N. Menguy, D. Mercier, P. Marcus, M. Fontecave and V. Mougel, *Nature Materials*, 2019, **18**, 1222-1227.
50. Z. Cai, Y. Zhang, Y. Zhao, Y. Wu, W. Xu, X. Wen, Y. Zhong, Y. Zhang, W. Liu, H. Wang, Y. Kuang and X. Sun, *Nano Research*, 2019, **12**, 345-349.
51. M. Gattrell, N. Gupta and A. Co, *Journal of Electroanalytical Chemistry*, 2006, **594**, 1-19.
52. K. C. Poon, W. Y. Wan, H. B. Su and H. Sato, *Rsc Advances*, 2022, **12**, 22703-22721.
53. M. R. Singh, J. D. Goodpaster, A. Z. Weber, M. Head-Gordon and A. T. Bell, *Proceedings of the National Academy of Sciences*, 2017, **114**, E8812-E8821.
54. C. G. Vayenas, R. E. White and M. E. Gamboa-Aldeco, *Modern Aspects of Electrochemistry*, 2008.
55. N. J. Firet and W. A. Smith, *ACS Catalysis*, 2017, **7**, 606-612.
56. J. Rosen, G. S. Hutchings, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos and F. Jiao, *ACS Catalysis*, 2015, **5**, 4293-4299.
57. E. Jeng and F. Jiao, *Reaction Chemistry & Engineering*, 2020, **5**, 1768-1775.

Data availability statement

Manuscript title: Radiation-assisted electrochemical reduction of CO_2 to CO

Manuscript Authors: Ryan P. Morco, Luis A. Diaz and M.M. Ramirez-Corredores

Manuscript Ref.: SE-COM-04-2024-000484

Data availability about data, software, or code supporting the results reported in the above referenced article manuscript is covered by the regulatory framework of the Idaho National Laboratory. All these are stored on secure servers with limited access to authorized personnel only.