



Exploring oxygen depolarized cathodes for zero-gap CO₂ electrolysis[☆]

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ABSTRACT

The electrochemical reduction of CO₂ to CO represents a pivotal step towards electrification of industries and Power-to-X strategies, however, industrial implementation remains limited by electrode flooding, salt accumulation, and unstable operation at high current densities. Herein, we demonstrate the use of oxygen depolarised cathodes (ODC), that are established and well-proven in chlor-alkali electrolysis, as a robust alternative electrode for CO₂ electroreduction under industrially relevant conditions. Notably, ODC exhibits superior mechanical durability, electrical conductivity, and flooding resistance enabling stable operation in membrane electrode assembly configuration over a wide current density range. By conducting a systematic tuning of both reactor temperature and CO₂ humidification, we identify that a delicate balance of water management and cation transport is critical for sustained performance. Stable operation was achieved at 100 mA/cm² and 200 mA/cm² with CO Faradaic efficiencies of 97% and 95% respectively over 24 h using a 0.1 M KHCO₃ anolyte. At 300 mA/cm², an intermittent electrolysis strategy with periodic current relaxation extended operation to 100 h maintaining 70% CO selectivity. These findings demonstrate the feasibility of using ODC as scalable and durable cathode for CO₂ electrolysis to CO and adapting operational conditions to achieve the industrially relevant deployment.

1. Introduction

Modern industrial processes remain dependent on precursors and energy from conventional fossil fuel derived resources, resulting in substantial greenhouse gas emissions and continued reliance on non-renewable carbon sources [1–3]. Transitioning from this linear ‘Take-Make-Waste’ paradigm towards an electrified circular carbon economy [4,5] offers a pathway to decouple chemical manufacturing from conventional resources by enabling continuous recycling of waste and emissions into the production chain. Accordingly, CO production via CO₂ electrolysis in a zero-gap electrolyser is a key step towards this future, due to its economically viability [6–8], and versatility as a feedstock for downstream valorisation to value-added products, through the Fischer-Tropsch process, carbonylation [9,10], hydrogenation [11–13] and further electrolysis [14–16]. However, industrial implementation of CO₂ electroreduction (CO₂RR) depends on optimising

stability, selectivity, productivity and energy efficiency to achieve practical and cost effective performance.

To meet these performance metrics, gas diffusion electrodes (GDE) have proven to be a key component to enable continuous CO₂ electrolysis at high current densities as compared to batch cells [17,18]. However, the traditional GDE architecture is prone to flooding, particularly at electrode heights exceeding 30 cm due to hydraulic pressure differences [19]. Moreover, large electrode surfaces may suffer from mechanical instability [20] and localised degradation due to uneven reaction environments which can lead to non-uniform electrochemical activity. The oxygen depolarised cathode (ODC), long-established in chlor-alkali industries, represents an industrially proven solution owing to its high electronic conductivity, mechanical robustness and tolerance to elevated hydraulic pressure [21,22]. Moreover, commercial availability of ODC provides consistent quality control and reliable supply, making them well suited for industrial level implementation. Notably,

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most ODCs employ silver-based catalysts that are intrinsically active towards CO₂ electrolysis to CO, making them a good candidate for investigation. Recently, ODC from several manufacturers have been demonstrated for CO₂ electrolysis within various configurations such as three-chamber setup [23], falling film design [19] and membrane electrode assembly (MEA) configuration, [24] but studies implementing the use of ODC in a zero-gap configuration operating at high current density and how to extend the stable operation remain limited.

Here, through strategic fine-tuning of the electrolyser operating conditions, we transform the ODC into a durable and resilient cathode for zero-gap CO₂ electrolysis, achieving steady performance at current densities as high as 300 mA/cm². The electrode shows stable operation across a wide operational range of current density due to the enhanced resistance to liquid flooding at the cathode-membrane interface. Through 24 h electrolysis, we demonstrated that the dominant deactivation causes are electrolyte saturation and salt crystallisation within the porous structure of the electrode. Nevertheless, it was discovered that a systematic variation of operating parameters could mitigate this: elevated reaction temperatures mitigate flooding by enhanced water removal, whereas controlled humidification aids in dissolving accumulated salt. Moreover, by introducing a dynamic intermittent electrolysis operation, stable performance was extended to 100 h at industrially relevant current density of 300 mA/cm², maintaining 70% CO faradaic efficiency at a cell potential of 3.4 V with 0.1 M KHCO₃ as anolyte. These results establish a practically competitive CO₂RR electrolysis platform ready for commercial by adopting technologies from allied electrochemical systems such as ODC. In summary, these findings highlight that long-term stability and selectivity in zero-gap CO₂ electrolysis are governed by the delicate balance between water management and ion transport within the electrode architecture.

2. Materials and methods

All experiments were conducted using Type-I ultrapure water (18.2 MΩ) sourced from Merck Millipore synergy, USA. CO₂ (N48, Air Liquide) was fed into the cathode at 35 S.mL/min for 100 mA/cm² and 55 S.mL/min for higher current densities using a mass flow controller (Aalborg DPC). The gas was bubbled through a vial containing Type-I ultrapure water (Merck Millipore synergy, USA) the temperature of which was regulated through a thermocouple (Ebro GFX460, Belgium). The gas was bubbled for 30 min to attain saturation and reach desired temperature before initiating experiments. Moreover, the distance between the humidifier and reactor was made as short as possible to avoid condensation along the way. The reactor was placed on a heating plate (VWR VHP C7, Belgium) and temperature was observed using a multimeter (Profile PIN116). A custom gas liquid separator was used to collect any liquid, and the product gas was then analysed using a gas chromatogram calibrated for CO, H₂ and CO₂ gases with a thermal conductivity detector (Shimadzu 2014 GC, Ar gas carrier – α1, Air Liquide). IrOx coated stainless steel (Feynman Dynamics) was used as the anode. 0.1 M KHCO₃ (>99.5%, Chem-Lab, Belgium) was used as anolyte and pumped at 5 mL/min. PiperION® 40 μm self-supporting AEM (Versogen, USA) was used as the membrane of choice for all experiments and was activated in 1 M KOH (>85%, Chem-Lab, Belgium) solutions. A schematic of the setup is given in Fig. S1.

Silver coated GDEs were prepared by air-spraying Ag ink onto Sigracet 39BB (SGL Carbon, Ion Power), named as Ag@Sigracet. The ink, containing Ag nanopowder (99.8%, >100 nm, Sigma Aldrich) and Sustainion XA-9 ionomer (in 5w/w% ethanol, Dioxide materials) in a 19:1 (w/w) ratio, was diluted with isopropanol (99.8%, Chem-Lab Belgium) and sonicated for 30 min. Spraying was performed at 60 °C using N₂ as carrier gas, yielding a uniform Ag loading of 1 mg/cm² confirmed by weight difference. The ODC samples were manufactured and supplied by De Nora using the company's proprietary catalytic slurry-based electrode fabrication process, which includes the preparation of a controlled-viscosity catalyst slurry, homogenization of the

mixture to ensure uniform particle dispersion, and deposition onto the carbon-based substrate through a thickness-controlled coating step. The coated substrates were then subjected to a defined drying and thermal treatment sequence to achieve the targeted layer thickness, porosity, and adhesion characteristics. An electrolyser of 4 cm² working area with serpentine flow fields integrated into the current collectors made of stainless steel was used for all experiments. All electrochemical experiments were done with a PARSTAT 4000 potentiostat, using chronopotentiometry method. Intermittent electrolysis was done by defining a sequence consisting of high current density (300 mA/cm², 58 min) and low current density (100 mA/cm², 2 min), which was repeated over the course of 100 h.

SEM imaging was done using Thermo Fischer Scientific Quanta FEI 250 at acceleration voltage of 15–20 kV. Contact angles were measured and analysed using OCA 15EC and DataPhysics software with a droplet volume of 10 μL. Liquid permeability was conducted using an in-house setup. Each substrate was mounted onto a custom-designed two-chamber test cell. The upper chamber was completely sealed and connected to a pressure meter (Greisinger GMH3111Ex, Germany) to monitor internal pressure. It was also linked to a pressurised closed liquid reservoir, with pressure regulation achieved by controlling the gas supply to the reservoir via a needle valve. By gradually increasing the pressure, the point at which the liquid first permeates the GDL (breakthrough) was recorded, as well as the rate of liquid permeation over time using a balance. Also, water was collected and weighed at the gas-liquid separator vial before and after experiments. Potassium crossover was measured by flushing the cathode with MilliQ water after experiments and conducting ICP-MS (Agilent 7850) analysis. The water crossover and potassium crossover was then calculated similar to our previous study [25].

3. Results and discussions

3.1. Humidification temperature matters

Initially, the ODC was evaluated in a 4 cm² zero-gap electrolyser with exchange-MEA configuration, feeding humidified CO₂ at room temperature. As shown in Fig. 1a, at 100 mA/cm², well pronounced oscillations of cell potential (between 2.8 and 3.8 V) were observed after 6 h of operation. Moreover, these fluctuations were correlated with the variations in the faradaic efficiency (FE) of the gas products: with the periods of increasing cell potential associated with enhanced CO formation, followed by a potential drop leading to a dominant hydrogen evolution. This oscillation was still observed even after 26 h of operation (Fig. S2) at the same reaction condition as shown in Fig. 1a.

Such oscillatory behaviour has been previously studied [26,27] and is attributed to the loop of salt clogging and flush-out. In details, salt crystallisation and accumulation within the GDE pores block CO₂ access to the catalyst layer, causing a shift in dominant charge carrier across the anion exchange membrane (AEM) from (bi)carbonate to OH[−], which consequently leads to a drop in cell potential due to the lower membrane resistance for hydroxide crossover. Meanwhile, electro-osmotic drag of electrolyte from anode subsequently and temporarily floods the electrode inevitably causing hydrogen production. Nevertheless, as a result of the flooding, the crystallised salt are dissolved as such restoring CO₂ transport, which then shifts the majority charge carrier back to (bi) carbonate and consequently restores the cell potential and CO₂ reduction. Insufficient humidification of the CO₂ stream or electrolyte flooding of the GDL pores tends to perpetuate this cycle, resulting in an eventual loop of salt buildup and subsequent flushing out. However, once this pseudo-steady state is established, a vicious cycle of self-sustaining oscillation develops, disrupting a consistent CO₂RR [28].

Notably, this behaviour was absent in case of Ag@Sigracet with a silver loading of 1 mg/cm². As shown in Fig. 1b. At 100 mA/cm², Ag@Sigracet maintained a stable operation with ~97.7% FE of CO for 100 h with a minimal decline of 0.05%/h. The superior stability of

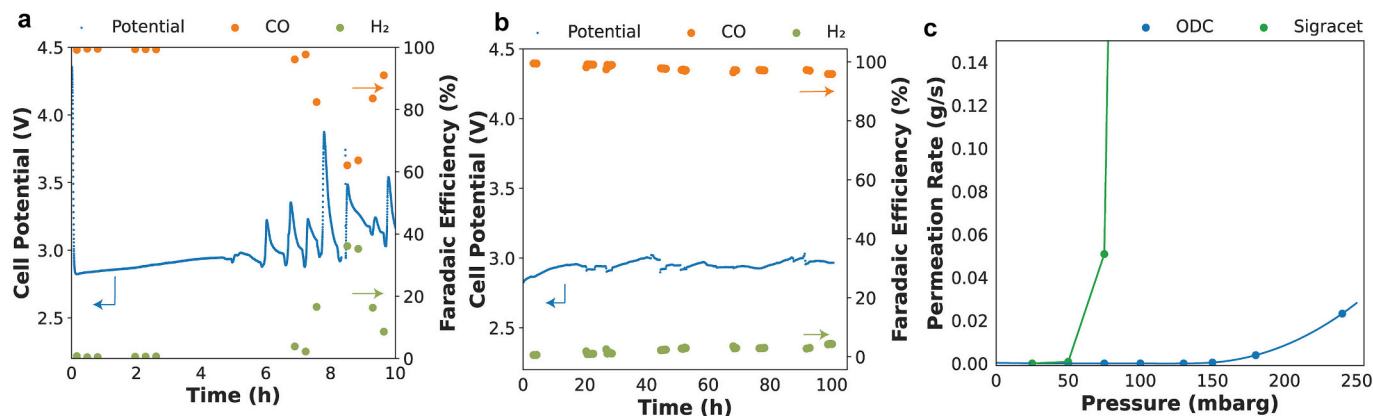


Fig. 1. Faradaic efficiencies of products and cell voltage at 100 mA/cm² for a) ODC b) Ag@Sigracet at 35 S.mL/min CO₂ and with 0.1 M KHCO₃ as anolyte. Both the humidifier and the cell was maintained at room temperature. c) Liquid permeability measurements of both electrodes in an in-house experimental setup.

Ag@Sigracet is mainly attributed to its distinct liquid permeability. As shown in Fig. 1c, Ag@Sigracet begins to break-through at 50 mbar(g) pressure difference with permeation increasing rapidly at higher value. In contrast, the ODC resisted flooding break-through until 150 mbar(g), and showed a gradual increase in permeation beyond this pressure. Even though the break-through pressure is likely reduced due to electro-wetting under applied potential [29], the ODC clearly exhibits significantly higher resistance to flooding. This property is essential in chlor-alkali electrolysis, where the cathode must withstand the hydraulic pressure of hot brine solution and prevent electrolyte flooding into the oxygen chamber [22]. However, in the case of CO₂RR in zero-gap cell this flooding resistance can inadvertently limit the removal of excessive accumulated salt, and compromise long-term stability. This leads to the strong oscillations observed at low current density (100 mA/cm²), whereas Ag@Sigracet with a lower breakthrough pressure can flush the

excessive salt buildup easily.

To mitigate oscillations due to salt buildup [26] at 100 mA/cm² for the ODC electrode, we explored humidification of the CO₂ feed at elevated temperatures. This should result in an increase of the vapour phase water content and will ultimately enhance salt dissolution and flushing within the electrode pores. The CO₂ feed was passed through a humidifier maintained at temperatures ranging from 30 °C to 60 °C, while the reactions itself are carried out at room temperature. As shown in Fig. 2b, operating at 30 °C humidification temperature (HT) largely suppressed the intense oscillations that were observed at room temperature HT (Fig. 2a), though minor fluctuations persisted near the end of the 24 h operation. At a HT of 40 °C as shown in Fig. 2c, the oscillations were subdued to micro-scale (~30–40 mV, Fig. S3) and the FE of products stabilised. Further increasing HT to 50 °C, resulted in the most optimal performance as seen in Fig. 2d. The cell potential and product

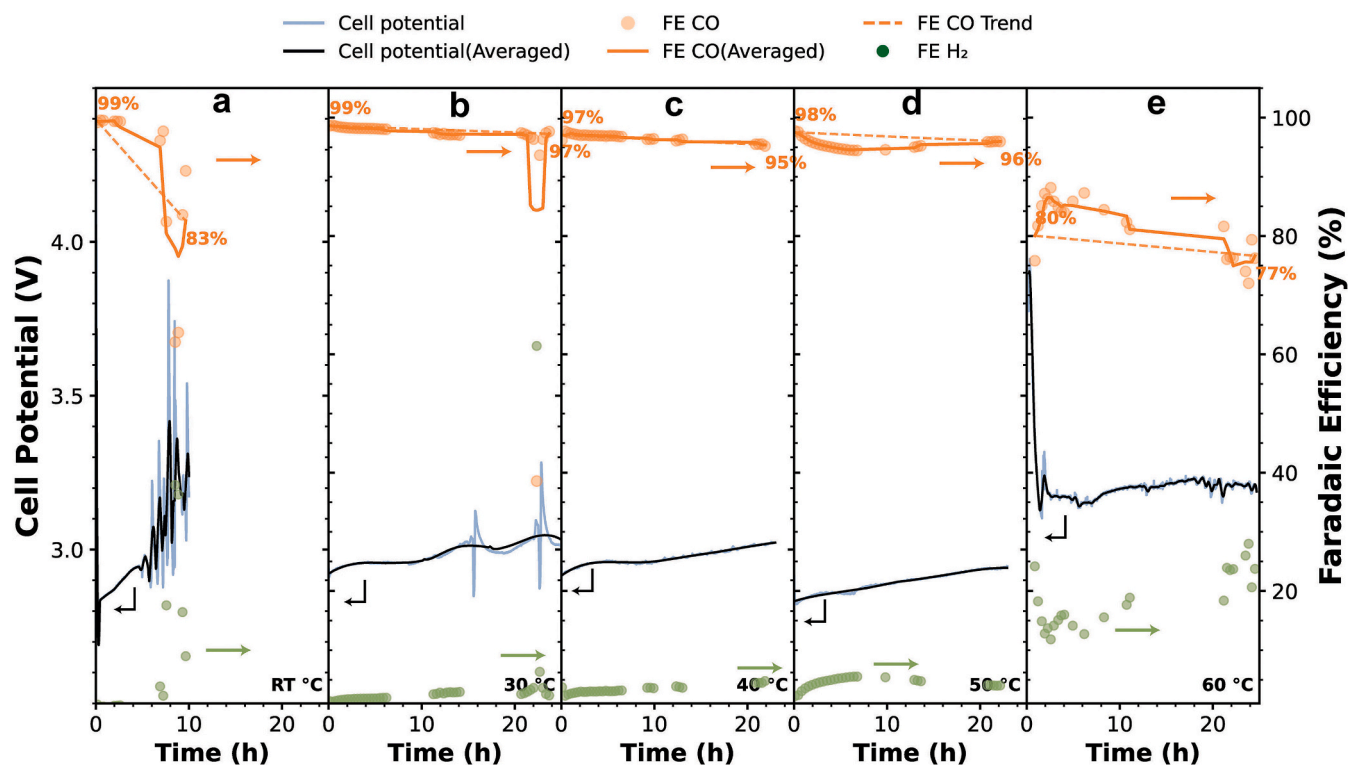


Fig. 2. Faradaic efficiency (FE) of CO and the corresponding cell potential using the ODC for room temperature CO₂ electrolysis with different humidification temperature at 100 mA/cm²: a) Room temperature b) 30 °C c) 40 °C d) 50 °C and e) 60 °C humidification temperature, All reaction were evaluated with 35 S.mL/min CO₂ flowrate and 5 mL/min 0.1 M KHCO₃ anolyte.

selectivity both remained constant over 24 h with only a 0.08%/h decline in FE_{CO} . However, further increasing the HT to 60 °C (Fig. 2e) induced renewed oscillations and a lower overall FE towards CO, mainly due to excessive flooding as a result of the too high water content, which again disrupted CO_2 access and electrochemical performance.

3.2. Reactor temperature matters

Following the optimisation of humidification temperature (HT) at 100 mA/cm², the study was advanced to the next phase, targeting a 200 mA/cm² operation. When increasing the current density from 100 to 200 mA/cm², the water required to conduct CO_2RR also doubles. Additionally, electro-osmotic drag at 200 mA/cm² drives more cation crossover from the anolyte, intensifying salt formation at the cathode [25]. As shown in Fig. 3a, room temperature CO_2 electrolysis operation at 200 mA/cm² with 50 °C HT (optimal conditions at 100 mA/cm²) still led to oscillations within 4 h and a rapid drop in FE of CO from 99% to 75% over 7 h. While increasing the HT to 60 °C subdued oscillations, the resulting FE of CO still sharply declined to 47% after 24 h. Further increasing HT to 70 °C and to extreme condition at 90 °C (Fig. S4) reintroduces oscillation again whilst overall CO selectivity remains significantly decreased. A closer look at the trend obtained at 60 and 70 °C HT in Fig. 3b and c respectively, reveals a different degradation path in selectivity: an increase in FE towards hydrogen and decrease in FE towards CO is observed within 5 h after which oscillations due to usual GDE pore blockage begin. We attribute this phenomenon to initial condensation of humidified water because the cell temperature is lower than that of the humidified stream. Such condensation in the pores of the GDL has also been observed in other electrochemical systems such as Polymer electrolyte membrane fuel cells (PEMFC) [30,31] due to lower local temperature, leading to flooding. This condensation ultimately floods the ODC pores and further triggers the oscillations.

To prevent this flooding from the humidified gas stream due to the condensation in the ODC pores, the reactor temperature was

subsequently increased. Elevated reactor temperature offers some advantages including improved reaction kinetics [32], enhanced CO_2 diffusion, and better membrane conductivity, thus reducing cell potential [33]. Such conditions are particularly relevant for pilot scale operation where stacks will heat up anyway due to resistive heating at high working potentials [34]. Unfortunately, increasing reactor temperatures can accelerate salt crystallisation due to water evaporation. Consequently, it is expected that even more gas phase humidification is required to counteract excess salt buildup before oscillations occurs.

By maintaining 60 °C as the lowest HT where oscillations were partially suppressed at 200 mA/cm², the reactor temperature (RT) was varied between 40 °C and 60 °C. As shown in Fig. 4 a, b, and c, the initial drop in FE of CO was suppressed due to reduced condensation, but the oscillations persisted especially at higher RT. As observed previously by Moss et al. [27] using *in-operando* XRD analysis and by Mikami et al. [26] using kymographic analysis, the persistence of oscillation signifies the formation of bicarbonate salts and this is mainly due to evaporation of water at the cathode at the higher reactor temperatures. Notably, at 50 °C RT, the system exhibited promising behaviour with reduced potential oscillations compared to 60 °C RT and a lower FE decline towards CO (0.75%/hr) compared to at 40 °C RT (1.29%/hr) and 60 °C RT (1%/hr). Further increase in RT will result in more intense oscillations and hence was not considered.

To further optimise the system, an RT of 50 °C was chosen as optimum and the humidification temperature was slightly adapted to 70 °C. This enabled stable operation at 200 mA/cm² for 24 h, achieving ~95% FE for CO (Fig. 4 d, and e), demonstrating that precise control by balancing both reactor and gas humidification temperature can optimise the CO_2RR performance at high current densities. Increasing gas-stream humidification helps prevent salt crystallisation; however, excessive humidification causes condensation and flooding. Similarly, flooding can be mitigated by raising the reactor temperature; however, excessively high temperatures may cause dehydration of the catalyst layer and membrane-electrode interface and enhanced salt formation.

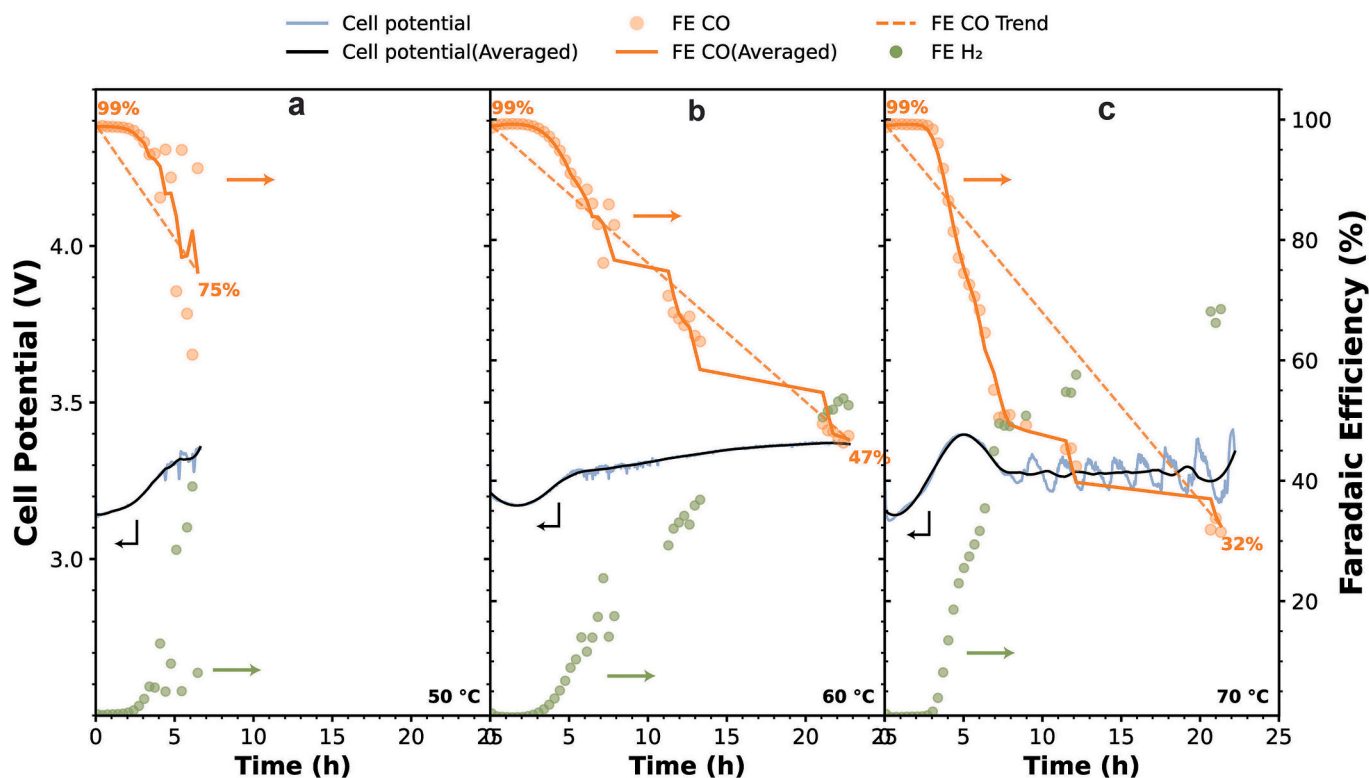


Fig. 3. Faradaic Efficiency (FE) of CO and corresponding cell potential at 55 S.L/min CO_2 flowrate and 5 mL/min 0.1 M $KHCO_3$ anolyte flow using the ODC at room temperature for a 200 mA/cm² electrolysis at a) 50 °C, b) 60 °C, c) 70 °C humidification.

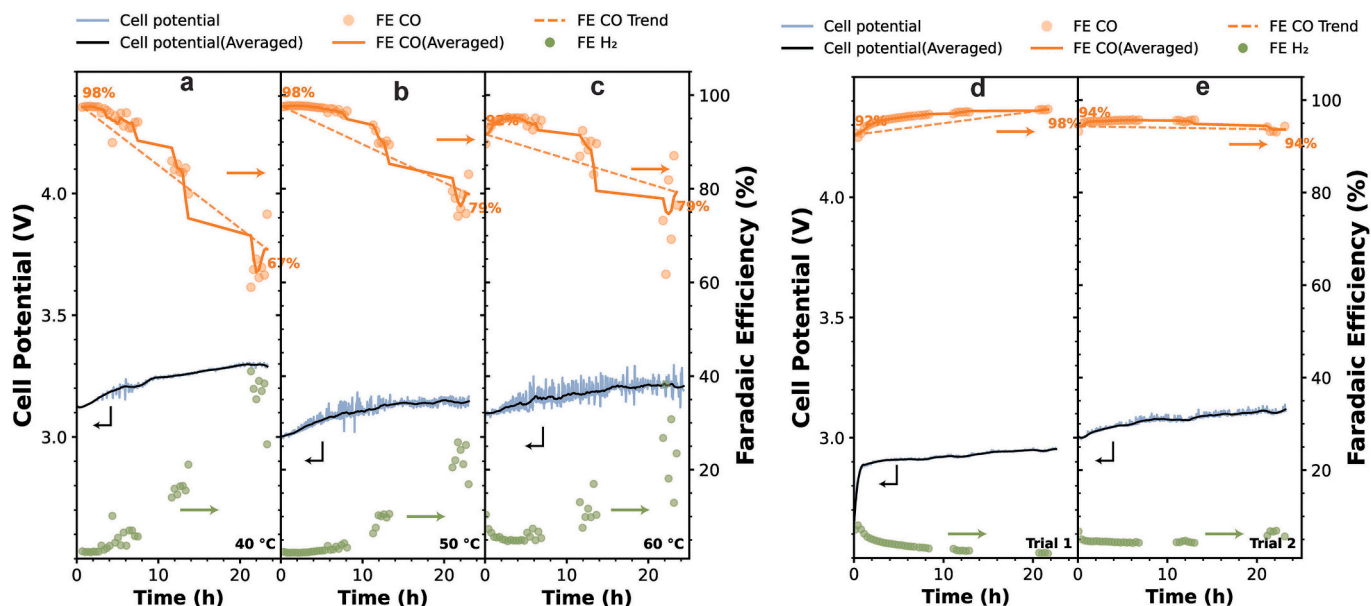


Fig. 4. Faradaic efficiency (FE) of CO and cell potential at 55 S.mL/min CO_2 flowrate and 5 mL/min 0.1 M KHCO_3 anolyte flow using the ODC at 200 mA/cm^2 electrolysis and 60 °C humidification temperature with a) 40 °C b) 50 °C and c) 60 °C reactor temperature and d),e) at 70 °C humidification temperature and 50 °C reactor temperature over two trials.

The major advantage of the ODC arises from the fact that at higher current densities, when the water permeation through the membrane increases [35], the greater breakthrough pressure for liquid electrolyte makes the ODC capable of resisting intense flooding of the cathode, maintaining CO_2 access to the catalyst layer at optimised conditions. As shown in Fig. S5, in the case of Ag@Sigracet, there was gradual flooding along with oscillations at 200 mA/cm^2 over 7 h of reaction, with a drop in FE towards CO at a rate of 3%/hr, at 50 °C RT and 70 °C HT. Moreover, as shown in Fig. S6, even at the most optimised condition for the Ag@Sigracet GDE, corresponding to 70 °C RT and room temperature HT, a performance decline of 2.38%/h towards FE for CO was observed,

albeit without oscillations. This is due to the lower liquid breakthrough pressure of Ag@Sigracet, which floods the cathode and blocks CO_2 from reaching the catalyst layer. Thus, for industrial operations involving high current densities, it is necessary to use a cathode with high breakthrough pressure which can avoid oscillations due to flooding, justifying our choice of the ODC electrode over the Sigracet for further evaluation.

3.3. Industrially relevant current density

After validating stable performance at 200 mA/cm^2 , we increased

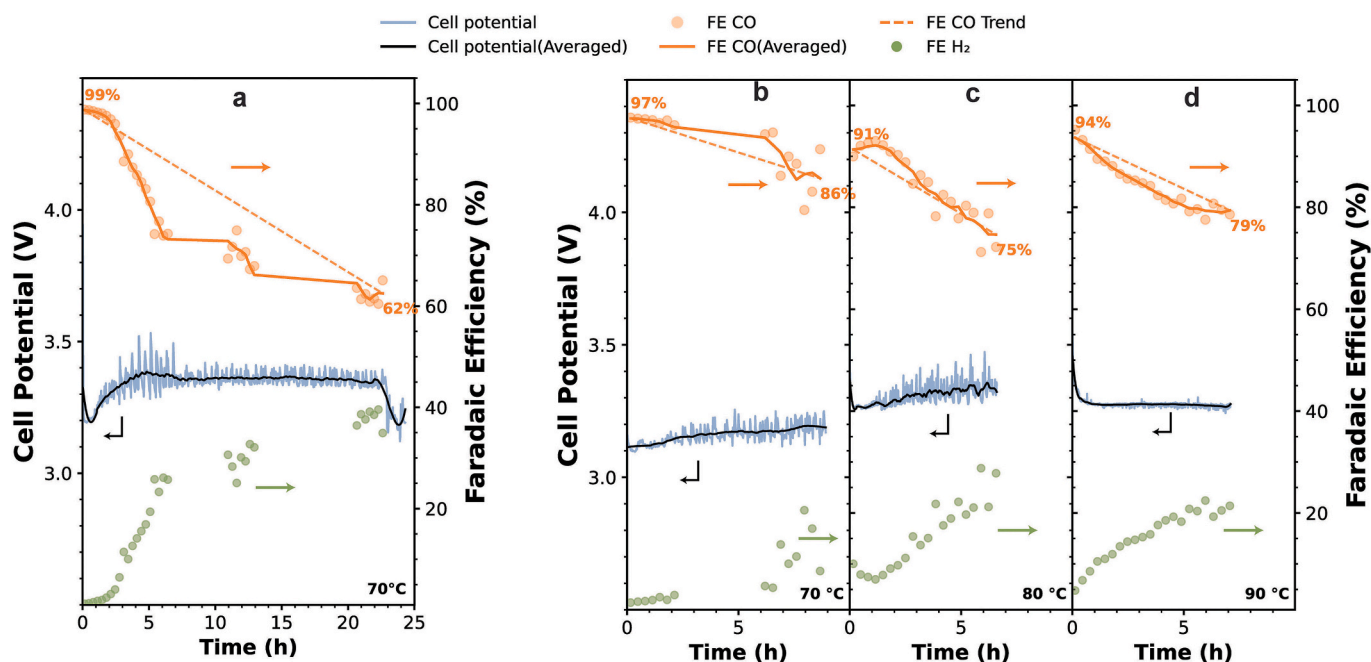


Fig. 5. Faradaic efficiency (FE) of CO and cell potential at 55 S.mL/min CO_2 flowrate and 5 mL/min 0.1 M KHCO_3 anolyte flow with the ODC at 300 mA/cm^2 electrolysis: a) 50 °C reactor temperature with 70 °C humidification temperature. b to d) 60 °C reactor temperature and with b) 70 °C c) 80 °C and d) 90 °C humidification temperature.

the operating current density to 300 mA/cm². Interestingly, upon operating at 300 mA/cm² with 50 °C RT and 70 °C HT, the previous optimal conditions, no longer ensures a stable operation, and a 1.54%/h decline in FE_{CO} was observed (Fig. 5a). An initial decrease in CO selectivity suggested water condensation within the electrode at this high current density, as stated in previous sections. A lower anolyte concentration can decrease the electro-osmotic drag due to cation crossover, however, a corresponding increase in cell potential without any significant mitigation of performance decline was observed, discarding the possibility to lower the concentration to improve performance (Fig. S7). To offset this, the RT was raised to 60 °C, meanwhile varying the HT between 70 °C and 90 °C to find a stable operation condition, the results of which are shown in Fig. 5b to d. In all these cases, micro-oscillations were still present and a decrease in CO selectivity over longer periods of time was persistently observed. At 90 °C HT, the cell potential remained stable, however, despite improved potential stability, the FE_{CO} declined rapidly at a rate of 2.14%/h. Thus, not only a precise control of humidification and reaction temperature is required, but at such high current densities it is necessary to take pro-active steps during electrolysis to maintain stable reaction.

To enhance the stability at high current density, we introduce a dynamic intermittent electrolysis with periodic current relaxation cycles. During extended operation, continuous electrolysis promotes gradual salt buildup within the GDE pores, which eventually will trigger oscillations. Temporarily lowering the current allows sufficient humidity from CO₂, to partially re-flood the electrode, dissolving and removing built up salts thereby restoring stable operation. Additionally, the reduced electric field during the low current phase facilitates (bi)carbonate anion transport back to the anode and decreasing the presence of salt forming ions at the cathode [36]. This strategy enables continuous operation under industrially relevant conditions by mitigating electrode degradation and oscillatory behaviour [37] without fully interrupting production but maintaining product generation albeit periodically at lower rates.

Using this intermittent electrolysis strategy, the experiment was extended to 100 h, achieving an active operational period of 96.6 h at 300 mA/cm². Long term operations were conducted at both 60 °C and

70 °C RT, with HT maintained at 90 °C as shown in Fig. 6a and b respectively. In both cases, an initial decline in FE towards CO of ~24% over the first 24 h was observed, after which the FE stabilised further decreasing at a low rate of 0.12%/h and 0.08%/h for the remainder of the operation at 60 °C and 70 °C HT, respectively. At 70 °C HT, the cell potential remained stable at 3.4 V throughout the electrolysis. The initial drop in FE in the first 24 h followed by a stabilisation can be attributed to a transient and dynamic cation crossover through the anion exchange membrane as observed previously by Gyenes et al. [38]. An initial surge in cation transport from the anode to cathode leads to temporary GDE saturation with electrolyte that progressively floods the cathode and decreases the FE towards CO. Once the cation transport reaches its equilibrium crossover rate, a cation balance is established and sustained CO₂RR is maintained leading to stable CO production rate. To control the reduction in product efficiency in the first 24 h, the study was repeated with 70 °C RT and 80 °C HT. As observed in Fig. S8, even though the average FE towards CO persisted above 80%, huge oscillations were observed in the FE, due to insufficient humidification at the cathode and intermittent electrolysis could not suppress the salt formation at cathode on its own.

3.4. Post-mortem analysis

To further understand the difference in performance between Ag@Sigracet and the ODC, the cathodes were characterised using contact angle analysis to measure the apparent hydrophobicity of the surface and SEM micrography to study the morphological differences. A comparison of the ODC catalyst surface with the Ag@Sigracet (Fig. S9b and S9a respectively) reveals a more uniform and finely dispersed distribution of Ag particles in the ODC. This enhanced dispersion facilitates greater exposure of catalytic sites at the reaction boundary, improving conversion rates at high current densities [39]. Moreover, as shown in Fig. S9c, after 100 h of electrolysis the ODC surface exhibited agglomerated clusters of smaller Ag particles, with an average cluster ~33% larger than the pristine state (Fig. S10a), indicative of morphological changes driven by prolonged electrochemical stress. This is consistent with degradation mechanisms such as coarsening or Ostwald ripening,

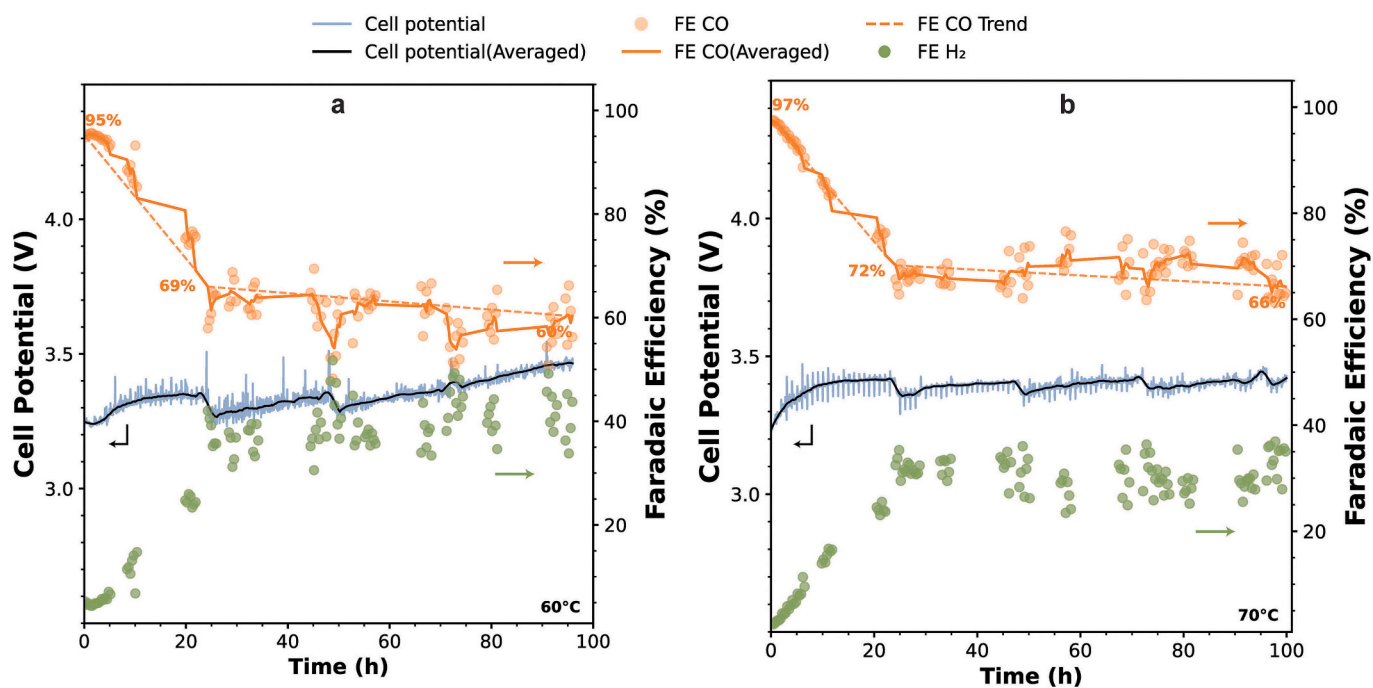


Fig. 6. Faradaic efficiency (FE) of CO and cell potential at 55 S.mL/min CO₂ flowrate and 5 mL/min 0.1 M KHCO₃ anolyte flow with the ODC at 300 mA/cm² electrolysis and 90 °C humidification at a) 60 °C and b) 70 °C reactor temperature.

where Ag dissolution and redeposition occurs under dynamic flooding-drying cycles [40–42]. Additionally, as shown in Fig. S10b and S10c the contact angle of the ODC increased from 133° to 144° reflecting an increased hydrophobicity after extended operation. This effect is presumed to be due to migration of PTFE particles or due to more exposed carbon surface at the cathode due to repeated flooding and drying cycles over 100 h of operation. The agglomeration of Ag particles was further investigated by analysing ODC samples that were not subject to intermittent electrolysis but were flooded within 4 h. An increase in contact angle to 138.5° was observed as shown in Fig. S11a from 133° for the fresh sample. Moreover, SEM analysis after 4 h also revealed that the particles were beginning to be reshaped [43] into a coarser structure (Fig. S11c) compared to smoother particle surfaces (Fig. S11b) before operation. This suggests that agglomeration of silver particles is not due to deactivation over long-term intermittent electrolysis but rather due to operation condition and essentially the flooding-drying cycles. Furthermore, measurement of potassium crossover and water migration to cathode over 4 h of experimentation, shows that in the case of non-intermittent electrolysis, a higher migration of both species was observed (Table S2), which led to intense flooding and performance degradation over a short period of time without the proper mitigation of the reaction conditions [44,45]. Overall, despite these gradual morphological changes, the ODC maintains superior flooding resistance and electrochemical performance compared to conventional GDEs, demonstrating its strong potential as a durable and scalable cathode platform for industrial CO₂ electrolysis. Compared with previously reported systems (Table S1), the present results demonstrate the highest performance at current densities of 100 and 200 mA/cm². At 300 mA/cm², the performance remains comparable to that of other high performing systems reported in the literature despite the use of commercially available materials and without relying on complex catalyst or interface engineering.

4. Conclusion

This study demonstrates that ODCs from the chlor-alkali process can serve as a robust alternative cathode for CO₂RR to CO, particularly under industrial relevant conditions. Their flexibility, stability and flooding resistance allows electrolysis operation across a wide current density range while maintaining consistent performance. The key contributors for long term stability were identified to be water management and cation transport, both of which must be delicately balanced through precise control of humidification as well as reactor temperature. A balanced operational window enabled stable electrolysis across 100–300 mA/cm²: at 100 mA/cm² the system achieved 96% FE for CO over 24 h, while at 200 mA/cm² 95% FE for CO was maintained for 24 h at dilute anolyte concentrations. At 300 mA/cm², a stable long-term operation was realised through intermittent electrolysis with current relaxation extending total runtime to 100 h with 70% FE maintained after an initial 24 h stabilisation period. Post-mortem analysis showed changes in the size and distribution of silver particles, indicating a gradual morphological evolution under sustained electrochemical stress. In conclusion, ODC provides a scalable industry-ready cathode platform for high-rate CO₂ electrolysis where optimised water-ion balance and adaptive operational control are key to achieve stable, selective and efficient carbon conversion at scale. With the findings from this work, we strongly believe that adapted ODC in the future can be used to achieve pilot-scale relevant current densities for CO₂ reduction.

CRediT authorship contribution statement

Shankar Ram Ramakrishnan: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Yu Zhang:** Writing – review & editing, Supervision, Conceptualization. **Balamurugan Devadas:** Writing – review & editing, Supervision. **Giovanni di Berardino:** Writing – review & editing, Conceptualization. **Kavita**

Shivanagoud Patil: Writing – review & editing, Investigation. **Luca Riillo:** Writing – review & editing, Resources, Methodology. **Nick Daems:** Supervision, Project administration, Investigation, Funding acquisition. **Tom Breugelmans:** Supervision, Project administration, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.182228>.

Data availability

The (processed) data will be published and made openly and freely available through deposition in the Zenodo repository of the University of Antwerp and ELCAT Research Group.

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