Pulsed potential electrochemical CO_2 reduction for enhanced stability and catalyst reactivation of copper electrodes

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ABSTRACT

The electrochemical conversion of CO_2 is a promising route to fuels and feedstocks. One of the great challenges in employing copper-based electrodes towards the electrocatalytic reduction of CO_2 is the unsustainable production of hydrocarbons over time. In this study, we show that by introducing a periodic pulsed operational mode during controlled potential electrolysis using low pulse frequencies in the range of Hz, the stability of ethylene production can be greatly increased from less than 8 h to at least 16 h. Furthermore, the method enables the reactivation of catalysts already deactivated for ethylene production. A duty cycle of >80%, deployment of a flow cell set-up, and a negligible loss of charge from the short anodic pulses as compared to the charge during the CO_2 reducing cathodic pulses are important aspects of this pulsed electrolysis considering future application in real cell reactors.

1. Introduction

The electrochemical reduction of CO_2 (CO_2R) is of vast research interest as it presents an opportunity to combine the use of excess renewable energy with the production of valuable products or fuels from the greenhouse gas CO_2, thus closing the carbon cycle [1,2]. As first described by Hori et al. in the 1980s, copper is the most promising metal capable of catalyzing the reduction of CO_2 to higher hydrocarbons, (C_{2+} products) [3]. However, copper-based catalysts typically suffer from limited stability in terms of their activity towards hydrocarbon production [4–7]. Long-term stability thus remains a central challenge in the CO_2R to C_{2+} products. Herein, we apply pulsed potential electrolysis as one approach to increase catalyst stability. This approach is common in other subfields of electrochemistry, such as electroplating or sensing [8,9]. However, it has rarely been employed in electrocatalysis. Nevertheless, there have been a few attempts to use pulsed potential electrolysis in different variants. In the 1990s, Shiratsuchi et al. first noted the increased selectivity and stability of ethylene production as well as the suppression of hydrogen evolution over a span of 25 h with switches every 5 s between a cathodic and more anodic potential [10]. In 2005, Hori et al. suggested that the activity of copper electrodes could be restored by anodic polarization (−0.05 V vs. SHE for 5 min) [7].

Recently, Kimura et al. showed similar effects on copper foil electrodes through the introduction of potential pulses of large amplitude in the time range of milliseconds [11]. Additionally, they showed that the beneficial effect can be restored after temporarily suspending the anodic pulses [12]. Le Duff et al. applied pulsed voltammetry to achieve CO_2R on copper single crystals, which also leads to a suppression of hydrogen evolution [13]. Our group reported a method based on "pseudo-anodic" pulses [14]. These pulses aim to mildly change the potential in order to achieve a small anodic current at the cathode for a short period, as depicted in Fig. 1a. The magnitude of the necessary potential difference between the anodic regeneration pulse and cathodic working phase is surprisingly small, since a small anodic current can be produced while keeping the applied voltage well below the open circuit potential (U_{OCP}) of the equilibrated system. These pulses are thus referred to as being pseudo-anodic.

The underlying mechanism that enables pulsing to suppress hydrogen evolution in favour of stable ethylene production remains under debate. It has been postulated that an oxide layer as well as a specific surface structure can be produced during pulsed potential electrolysis [15–17]. The benefit of the pulses could hence be attributed to the well-established advantages of oxide-derived copper and the constant restructuring of the copper surface [18,19]. On the other hand,

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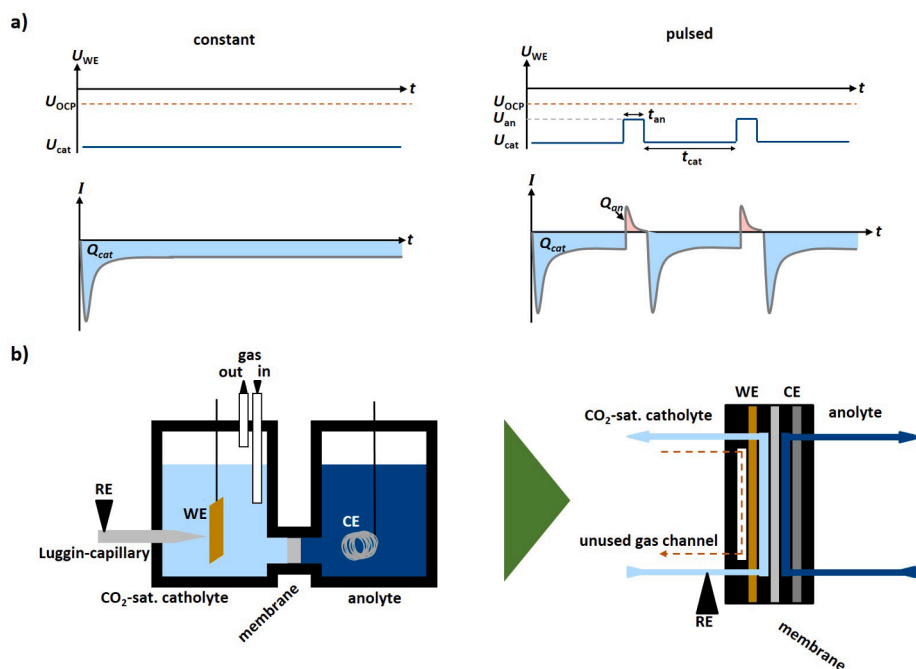*E-mail address:* functional.materials@uni-bayreuth.de (R. Moos).

Fig. 1. (a) Schematic depiction of the course of applied voltage (top) and measured current (bottom) in constant (left) and pulsed (right) electrolysis over time. In the constant case, a constant potential (U_{cat}) is applied. The current shows an initial maximum due to electrode polarization, before settling at a constant value. Introducing regeneration pulses (voltage U_{an}) results in periods of small anodic currents that alternate with the cathodic current phases. Note that U_{an} is below the open circuit potential U_{OCP}. Every time the potential is switched, electrode polarization reoccurs, resulting in a short-lived peak in the current. The anodic charge Q_{an} passed during regeneration is considerably lower than the cathodic charge Q_{cat} passed during working phases. (b) Schematic depiction of a sheet copper cathode operated in an H-cell (left) and a flow cell (right). Note that the commercial flow cell has a gas channel on the left for use when gas diffusion electrodes are operated. This channel remains unused as we utilized sheet copper electrodes in this study.

Kim et al. showed very recently that pulsing has a beneficial effect even if no anodic current is produced and the surface morphology is kept unchanged throughout the entire experiment [20]. They assume that increased CO availability is the key. It was also suggested that the deposition of carbon onto the electrode is prevented by pulsing [16]. Additionally, the switch in polarization may assist in desorbing hydrogen, which could otherwise block active catalytic sites (adsorption poisoning) [17].

To the best of our knowledge, all previous studies on pulsed CO_2R have been conducted in H-type cells or the like, where CO_2 is only accessible as a solute in the electrolyte. Recent advances in the field of CO_2R show that the most promising systems for industrial applications are likely to be flow cells operated with gas diffusion electrodes (GDEs), as they allow for a direct supply of gaseous CO_2 to the reaction site [6,21,22]. There are large conceptual differences between flow cells and H-type cells that could pose a problem with the application of pulsed potential electrolysis in flow cells [22]. It has been observed that part of the copper surface dissolves during the anodic pulses, and is redeposited on the cathode as copper oxide [16]. The electrolyte flow along the catalyst surface in a flow cell may flush away dissolved copper ions, disrupting the desired process. Thus, pulsed potential electrolysis must be evaluated under flow conditions anew.

The transition from sheet-like electrodes in a H-cell used in our previous studies [14,18] towards GDEs operated in a flow cell geometry necessitates a complete change in the experimental set-up, including but not limited to: different electrochemical cell, changes in the peripheral cell set-up to facilitate media flow, and a different kind of working electrode. Thus, by operating the original sheet copper instead of GDEs in the new flow cell set-up, we investigate an intermediate step of the transition, accounting for pulsed potential electrolysis while at the same time mimicking our previous studies in consideration of electrode material and electrolyte composition. The new electrochemical cell is already designed for GDE operation. However, as sheet copper was used in this intermediate step, the cathodic gas channel was not utilized, and the catholyte was saturated with CO_2 instead (Fig. 1b). It has to be noted that the presented data does not allow for direct conclusions to be drawn regarding GDE usage.

2. Experimental

All aqueous solutions were prepared using ultrapure water (Milli-Q®, resistivity 18.2 MΩcm). Materials and methods are largely based on previously reported procedures [14].

2.1. Preparation of electrodes

Sheets of deoxygenized high phosphorous copper (Cu-DHP, DIN EN 1172:2012-02, Eisenmetall, Thyssenkrupp Schulte GmbH; 0.5 mm thickness) were used as working electrodes. Analysis of the electrode material (SEM, XRD, ICP) confirmed the data reported previously [14] and the DIN standard. We identified this copper material as a suitable catalyst for ethylene production in non-GDE configurations in previous studies [23]. Moreover, this type of copper is available in large quantities as a certificated DIN material from industrial suppliers. The sheets were cleaned by polishing with SiC sandpaper (2400 and 4000 grit) and then etched in 0.3 M $(NH_4)_2S_2O_8$ (Honeywell Fluka, >98%) at 80 °C for 2 min. After each step, the electrodes were rinsed and then ultrasonicated in ultrapure water.

2.2. Electrolysis experiments

All electrolysis experiments were carried out in a flow cell (modified Micro Flow Cell, Electrocell; exposed electrode surface area = 10 cm^2), using an Ir-MMO anode (Electrocell) and a Nafion membrane (N117, Ion Power GmbH). The reference electrode (Ag/AgCl (3 M KCl), Metrohm) was incorporated via a T-piece into the catholyte feed. All voltages are reported vs. Ag/AgCl. The catholyte consisted of a CO_2-saturated 0.1 M KHCO$_3$ (Sigma Aldrich, >99.95%) solution (pH 8.5 as prepared), and the anolyte was a 1 M KHCO$_3$ (Sigma Aldrich, >99.7%) solution (pH 8.3 as prepared). 800 mL of each were cycled through the cell via magnet drive rotary pumps (M1, March Pumpen GmbH & Co. KG). CO_2 saturation of the catholyte was achieved by bubbling ultrapure CO_2 (Rießner, grade 5.5) through the catholyte reservoir for at least 15 min. The applied potential and current were controlled by a potentiostat (Metrohm Autolab PGSTAT302N) and products were quantified with a gas chromatograph (Trace 1310, Thermo Fisher). The product distribution of electrolysis processes is primarily evaluated by calculating the
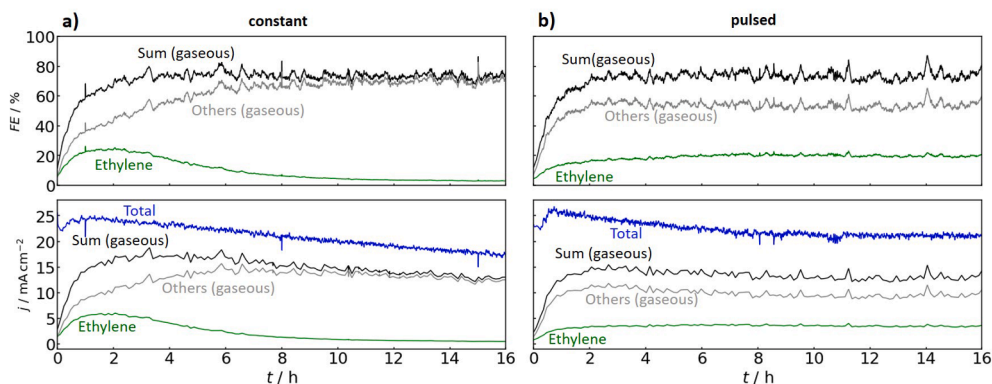
Fig. 2. Faradaic efficiencies (top) and current densities (bottom) for (a) a constant potentiostatic (-1.38 V) and (b) a pulsed potential (25 s at -1.38 V; 5 s at -1.0 V) electrolysis. The total current refers to the current as measured by the potentiostat, while the sum refers to the sum of all gaseous products as determined by GC analysis (H_2, CO, CH_4, C_2H_6, C_2H_4).

partial current densities and faradaic efficiencies (FE) for each product. It should be emphasized, however, that when calculating the faradaic efficiency for pulsed electrolysis, an additional factor, as previously reported, has to be accounted for as follows [14]. The faradaic efficiency is defined as the percentage of the total current that is used to produce each product. The amount of product is calculated via gas chromatography (GC) with a time resolution between individual samples of approximately 6.5 min. Therefore, the individual cathodic working phases lasting a few seconds cannot be resolved from the timescale of product quantification. This would then lead to artificially lowered FE values, as there is no product generation during the pseudo-anodic regeneration pulses. Therefore, when calculating FEs, they have to be corrected by the factor $(t_{an} + t_{cat})/t_{cat}$, where t_{an} represents the duration of a regeneration pulse and t_{cat} the duration of a working phase.

3. Results and discussion

As a benchmark, non-pulsed potentiostatic electrolysis with a constant applied voltage of -1.38 V (henceforth referred to as constant electrolysis conditions) was conducted over a duration of 16 h (Fig. 2a). In this operation mode, the high initial FE for ethylene of 26% drops to nearly zero within the first 12 h. The sum of the other measured gaseous components (CO, H_2, CH_4, and C_2H_6) increase proportionally to that loss, resulting in a stable sum of FEs for all measured gaseous products. The remaining 20% of the total FE that is not accounted for can most probably be attributed to liquid phase products, which were not quantified in this study [24]. The rapid rise of FE for all products during the initial stages is due to technical reasons, as the saturation of the catholyte with the products as well as the need to completely flush all the gas headspaces in the set-up requires some time. The trend for ethylene FE compares well to those from measurements performed in an H-cell [14]. The current density, both total and partial for ethylene, is, however, higher in the flow cell. This could be due to two factors. Firstly, the flow of electrolyte could improve reactant and product transportation. Secondly, the potential directly at the working electrode surface may differ between the two cell configurations. Such an offset is likely when changing cell geometry and thus electrode positioning, which affects the iR drop [25]. The cell resistance was determined to be approximately 7 Ω, and the resistance between reference and working electrodes was around 1 Ω. Based on this value and the observed current, an iR drop of a magnitude of 200 mV can be calculated.

Fig. 2(b) shows the results from pulsed electrolysis conducted under conditions similar to those of the previously described constant electrolysis (applied working potential of -1.38 V and a duration of 16 h). Additionally, however, the applied potential was changed every 25 s to the pseudo-anodic regeneration potential of -1.0 V, at which it was then held for 5 s before returning to -1.38 V. This potential is still far below
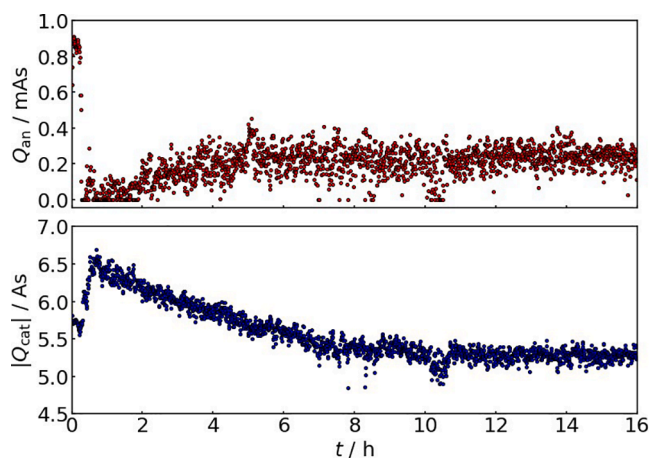

Fig. 3. Charge of each individual anodic regeneration pulse Q_{an} (top) and cathodic working phase Q_{cat} (bottom) throughout the course of the pulsed electrolysis (Fig. 2b). Note that the magnitude difference between the two panels is in the range of 10^4.

the measured open circuit potential of -0.137 V. The results show a constant FE for both ethylene and the sum of all other gaseous components, with no sign of decay in ethylene activity over 16 h. Comparing constant and pulsed electrolysis, the beneficial effect of pulsed electrolysis on the stability of ethylene production is evident. The maximum FE for ethylene (23%) is approximately 3% lower in pulsed than in constant voltage operation; this is within the variance observed between individual runs.

The total measured current densities during both constant and pulsed electrolyses show a decline over the first 6–8 h. However, while this continues to decrease over the course of the constant electrolysis, the current density reaches a stable plateau in the pulsed operation. One reason often considered for the general deactivation of Cu-based catalysts is the rearrangement of the copper surface and therefore a decrease in the number of active sites and facets [26]. The pulsed electrolysis appears to be able to stabilize the active catalyst facets, probably through active surface reconstruction, as proposed by Arán-Ais et al. [15]. In contrast, Kim et al. suggested that increased CO availability during pulsing is the key to better long-term performance [20]. It can be concluded from our results that pulsed potential electrolysis has a beneficial effect to the extent that ethylene production can be significantly prolonged, and that this also holds in a flow cell geometry.

To show the ratio of charges passed in the pseudo-anodic regeneration pulses and cathodic working phases, the respective charges Q_{an} and Q_{cat} for each pulse were compared (Fig. 3). The charge passed in a
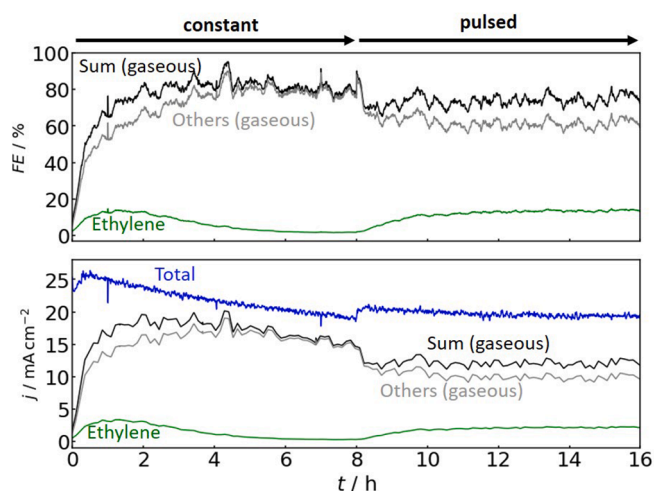
Fig. 4. Faradaic efficiency (top) and current densities (bottom) for a combined electrolysis, consisting of 8 h of constant potentiostatic (−1.38 V) electrolysis, followed by 8 h of pulsed electrolysis (25 s at −1.38 V; 5 s at −1.0 V).

working phase is approximately four decades higher than that passed in a regeneration pulse. In fact, the cumulative amount of anodic charge over the entire experiment only corresponds to 0.004% of the cathodic charge. The loss of charge due to the regeneration can therefore be considered to be negligible.

During each individual regeneration pulse, the current only remained anodic for a fraction of the period as a result of electrode polarization, before once again dropping below zero. This suggests that the regeneration period could in principle be shortened in order to further increase the duty cycle, without diminishing the desired stabilization effect. Note that in order to calculate Q_{an}, only the periods of truly anodic current (above zero) were included.

In order to further elucidate the potential that a pulsed operation can have in stabilizing the copper catalyst, a reactivation of an already deactivated catalyst was demonstrated. Fig. 4 depicts the course of an electrolysis in which 8 h of constant potential were followed by 8 h of pulsed operation. The parameters were chosen in accordance with the previous experiments. A drop in ethylene selectivity from FE 15% down to 2% within the first 8 h is followed by a significant recovery back up to 15% as soon as pulsing commences. At the same time, the sum of all other gaseous components drops as expected. The experiment demonstrates that introducing pulses to an electrolysis is not only capable of stabilizing, but even of reactivating the catalyst for ethylene production. This adds a new layer of significance to the pulse method, as it would allow activity to be restored during variable operation cycles (e.g. on/off cycle) that could arise as a result of the intermittency of available renewable energy or maintenance requirements.

The reasons for the beneficial effect of pulsed electrolysis are still unclear; thus, the investigation of surface changes during pulsed electrolysis would certainly be of interest. Since the configuration employed in this study is not suited for in situ analytics, the fundamental background of the method has yet to be investigated.

4. Conclusion

Herein, pulsed potential electrolysis for CO_2 electroreduction on copper catalysts was applied in a flow cell set-up for the first time. The beneficial effect on the long-term stability of ethylene activity was confirmed, despite the introduction of electrolyte flows and the change of geometry in comparison to commonly used H-type cells. In addition, it was shown that beyond stabilization, pulsed electrolysis was able to reactivate the ethylene activity of the catalyst after it had dropped to zero under constant voltage operation, thereby increasing the possibility

of new applications for this method. Finally, the loss of charge due to the regeneration pulses was found to be negligible. An important intermediate step in the transferal of pulsed electrolysis operation modes from the H-cell to the flow cell was therefore successfully demonstrated. Follow-up work employing these findings with CO_2R gas diffusion electrodes is underway.

CRediT authorship contribution statement

Yannick Jännsch: Investigation, Methodology, Writing - original draft, Writing - review & editing. **Jane J. Leung:** Methodology, Writing - review & editing. **Martin Hämmerle:** Supervision, Writing - review & editing, Funding acquisition. **Erhard Magori:** Methodology. **Kerstin Wiesner-Fleischer:** Writing - review & editing. **Elfriede Simon:** Writing - review & editing. **Maximilian Fleischer:** Writing - review & editing. **Ralf Moos:** Supervision, Writing - review & editing, 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.

Acknowledgements

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