

Pulsed Electrolysis with a Nickel Molecular Catalyst Improves Selectivity for Carbon Dioxide Reduction

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ABSTRACT: Pulsed electrolysis can significantly improve carbon dioxide reduction on metal electrodes, but the effect of short (ms-s) voltage steps on molecular electrocatalysts is largely unstudied. In this work we investigate the effect pulse electrolysis has on the selectivity and stability of the homogenous electrocatalyst $[\text{Ni}(\text{cyclam})]^{2+}$ at a carbon electrode. By tuning the potential and pulse duration we achieve a significant improvement in CO Faradaic efficiencies (85%) after 3 h, double that of the system under potentiostatic conditions. The improved activity is due to in-situ catalyst regeneration from an intermediate that occurs as part of the catalyst's degradation pathway. This study demonstrates the wider opportunity to apply pulsed electrolysis to molecular electrocatalysts to control activity and improve selectivity.

MAIN TEXT: Electrochemical carbon dioxide reduction (CO₂R) holds the potential to convert CO₂ to fuels and chemical feedstocks, utilizing renewable energy. Efforts are focused on developing new electrocatalysts and controlling the electrode-electrolyte interface with existing catalysts to understand and improve their catalytic behaviour.¹⁻⁴ Experiments are typically carried out under potentiostatic or galvanostatic conditions. However recent studies on metal electrodes have utilized pulsed electrolysis as a way to influence and improve reaction selectivity and stability in electrochemical CO₂R.^{5,6} There are multiple proposed effects of using a pulsed voltage depending on the system and pulse parameters used, from inhibiting catalyst poisoning,⁷⁻¹¹ surface oxidation or roughening,^{7,8,11-14} rearrangement of surface coverage,^{13,15-17} and altering the local pH and CO₂ concentration at the electrode.¹⁸⁻²¹

While there are many pulsed studies on different metal electrodes for CO₂R, we are not aware of any where the impact of short (ms-s) voltage pulses is examined with homogenous molecular catalysts despite it offering a potential way to modify catalytic activity and stability. In this work we report a pulse electrolysis study on a homogenous molecular catalyst for CO₂R with an inert glassy carbon working electrode (GCE). Nickel cyclams (cyclam = 1,4,8,11-tetraazacyclotetradecane) are well studied both photo-²²⁻²⁴ and electrocatalysts for CO production in aqueous electrolytes.²⁵⁻³² Recently [Ni(cyclam)]²⁺ has also been found to be selective for CO production when used on gas diffusion electrodes in H-cells,^{33,34} and higher current density electrolyzers,^{30,35} notably even at low pH,³⁵ making efforts towards improving its activity and stability of particular interest.

Early experiments with [Ni(cyclam)]²⁺ were carried out with the catalyst adsorbed onto Hg electrodes, but more recently it has been shown that [Ni(cyclam)]²⁺ can also be used with a GCE.^{29,36} Here Faradic efficiencies are typically lower but the catalyst does not adsorb (Fig S2) creating a simpler molecular system to study the effects of pulsed electrolysis. Fig 1A shows a cyclic voltammogram (CV) of 1 mM [Ni(cyclam)]²⁺ in 0.5 M NaCl using a GCE. Under Ar the CV remains fairly featureless as hydrogen evolution obscures the Ni(II)/(I) couple in aqueous electrolyte.²⁹ Under CO₂ we see a significant increase in current at -1.5 V vs Ag/AgCl indicating CO₂R and the appearance of two small anodic features at -1.3 V (i) and -0.5 V (ii), assigned to the oxidation of deactivated catalyst species [Ni(cyclam)(CO)]⁺ and further irreversibly reduced Ni(0) carbonyl respectively.³⁷ The formation of [Ni(cyclam)(CO)]⁺ as a result of the high CO binding

constant to $[\text{Ni}(\text{cyclam})]^{2+}$ ($K_{\text{CO}} = 7.5 \times 10^5$, $K_{\text{CO}_2} = 16$) has been proposed to be the cause of the low stability and selectivity's of the catalyst when used at both GCE and gas diffusion electrodes.^{33,35,37} More widely CO poisoning and overreduction of intermediates has been proposed to limit stable electrochemical CO_2R in a range of molecular catalysts, with metal centers including Ni,^{38,39} Fe,^{40,41} Co etc.⁴²⁻⁴⁴ Remediation methods have included removal of CO with scavengers or increased gas flow,^{35,37} modifications to the catalyst structure,⁴⁰⁻⁴⁴ or instating long periods (minutes-hours) for recovery/regeneration, which only leads to a temporary recovery in activity.^{33,35}

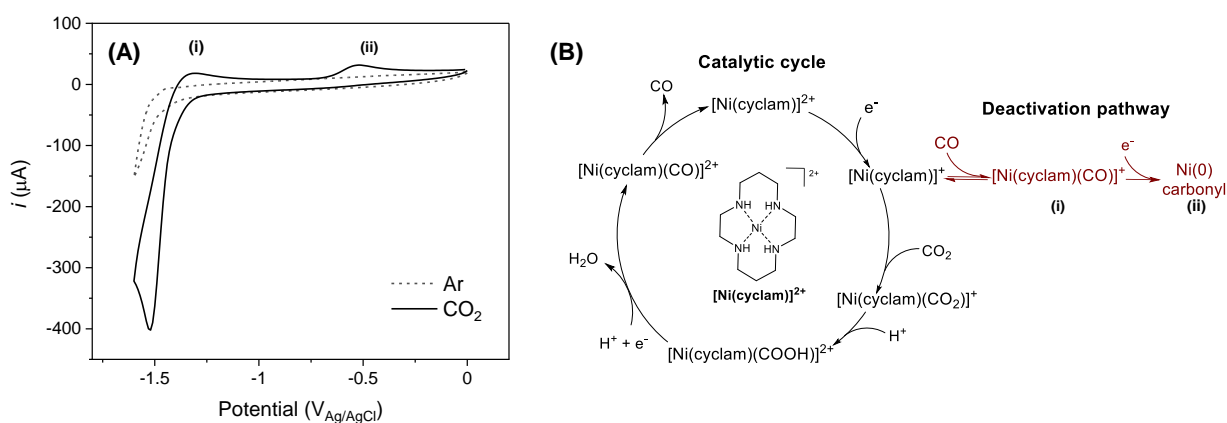


Figure 1. (A) CV of 1 mM $[\text{Ni}(\text{cyclam})]^{2+}$ in 0.5 M NaCl at a GCE at 1 V/s (0 V to -1.6 V to 0 V) under Ar and CO_2 vs. Ag/AgCl, Pt counter separated by vycor frit, recorded without iR compensation. Plotted using IUPAC convention (B) Reported catalytic cycle and deactivation pathway of $[\text{Ni}(\text{cyclam})]^{2+}$.²⁹

In this work we incorporate of short 40 ms - 1 s asymmetric anodic pulse (E_A) throughout electrolysis to enable stable operation (see tables S1-3 and Fig S3-7 for chronoamperometry data). Fig 2 shows potentiostatic (denoted as Standard) and pulsed electrolysis experiments of 0.1 mM Ni(cyclam) in CO_2 saturated 0.5 M NaCl over 3 hours at a GCE. The standard electrolysis was held at a cathodic potential (E_C) of -1.6V vs Ag/AgCl throughout. For initial pulsed electrolysis studies E_C was held for 5s (t_C) before an anodic potential (E_A) of -1.0V vs Ag/AgCl was applied for 0.2s (t_A). The pulsed voltage profile led to a four-fold increase in selectivity for CO ($\text{CO}/\text{H}_2 = 2.42 \pm 0.10$), that was stable over three hours, compared with the standard run ($\text{CO}/\text{H}_2 = 0.63 \pm$

0.21). The pH of the electrolyte was measured before and after electrolysis, where a slight increase was observed post-electrolysis (from 6.3 to 7.8 (standard), 7.7 (pulsed)) in both the standard and pulsed run. Table S4 shows the total cell energy efficiency for CO₂ to CO of the pulse system is almost double that of the standard experiment demonstrating that any energy losses associated with the voltage pulse are offset by the increased FE for CO and higher CO production rate.

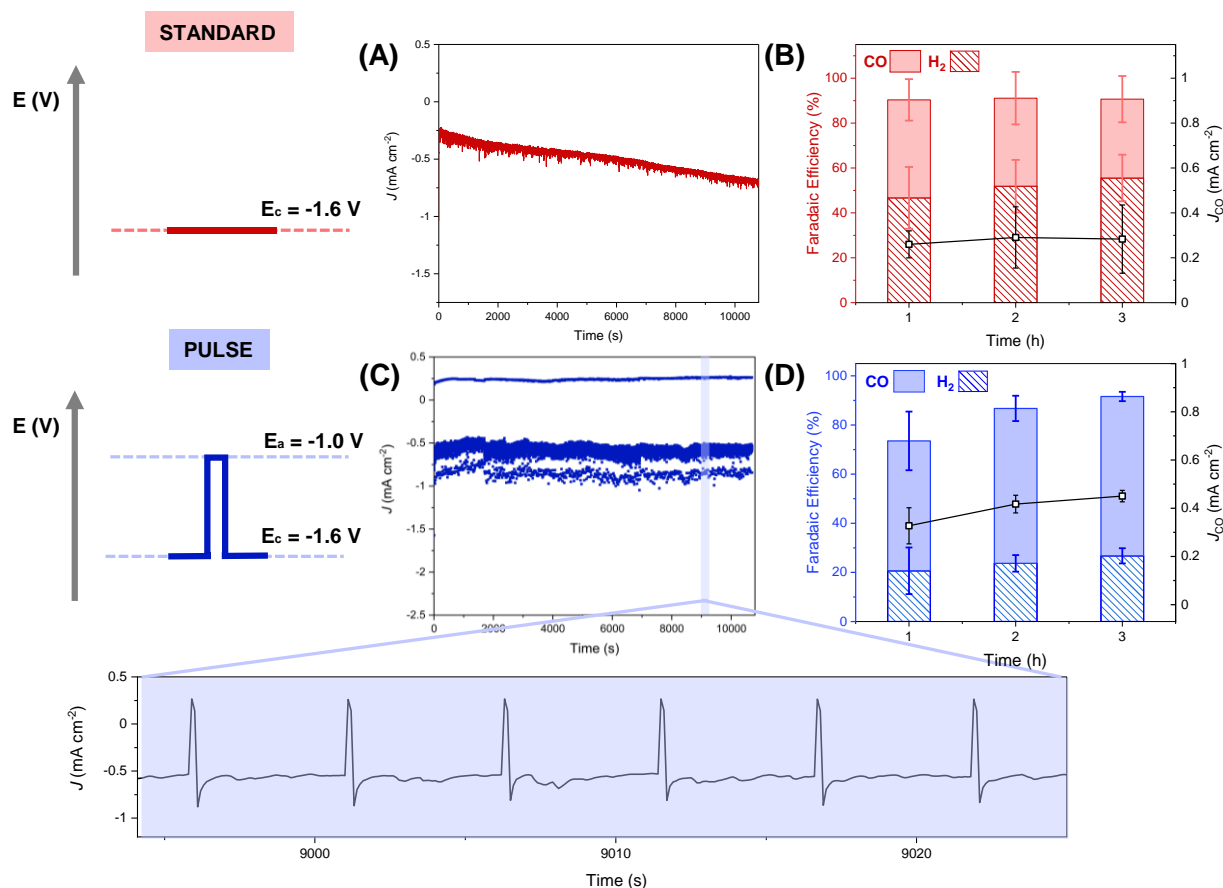


Figure 2. Comparison of standard ($E_c = -1.6$ V_{Ag/AgCl}) and pulsed ($E_c[t_c] = -1.6$ V_{Ag/AgCl} [5 s]; $E_a[t_a] = -1.0$ V_{Ag/AgCl} [0.2s]) electrolysis of 0.1 mM [Ni(cyclam)]²⁺ in 0.5 M NaCl(aq) over 3h. (A) Chronoamperometry trace of standard run (B) FEs and CO partial current densities of standard run (C) Chronoamperometry trace of pulse run (D) FEs and CO partial current densities of pulse run. A kinetic analysis of the fast response of the system upon pulsing can be found alongside Fig S8.

Fig 2A and Fig S9 show that the overall current density increases during a standard electrolysis experiment and that this is due to increased hydrogen evolution. XPS of rinsed GCE's after 3 hours

of either standard or pulse electrolysis show Ni on the GCE post standard electrolysis but not on the pulse electrolysis sample (Fig S10-12). The Ni XPS of the GCE post standard electrolysis does not match that of a powder sample of $[\text{Ni}(\text{cyclam})]^{2+}$ and an analysis of the Ni:N peak ratio from the survey scan (0.24 (post standard electrolysis GCE) and 2.36 ($[\text{Ni}(\text{cyclam})]^{2+}$). This shows that most of the deposited Ni is no longer coordinated to the cyclam ligand. Instead we assigned it to mainly $\text{Ni}(\text{OH})_2$ (see SI for details).^{45,46} Cyclam loss is proposed to occur following the reduction of $[\text{Ni}(\text{cyclam})(\text{CO})]^+$ to form Ni(0) carbonyl compounds, which may oxidize upon exposure to atmosphere.³⁸ An increase in hydrogen evolution following Ni(0) deposition is in-line with other studies on Ni based electrocatalysts^{37,38,47} and here we find that the GCE post standard electrolysis has a decreased onset potential for hydrogen evolution when used in a fresh NaCl electrolyte (Fig S14).

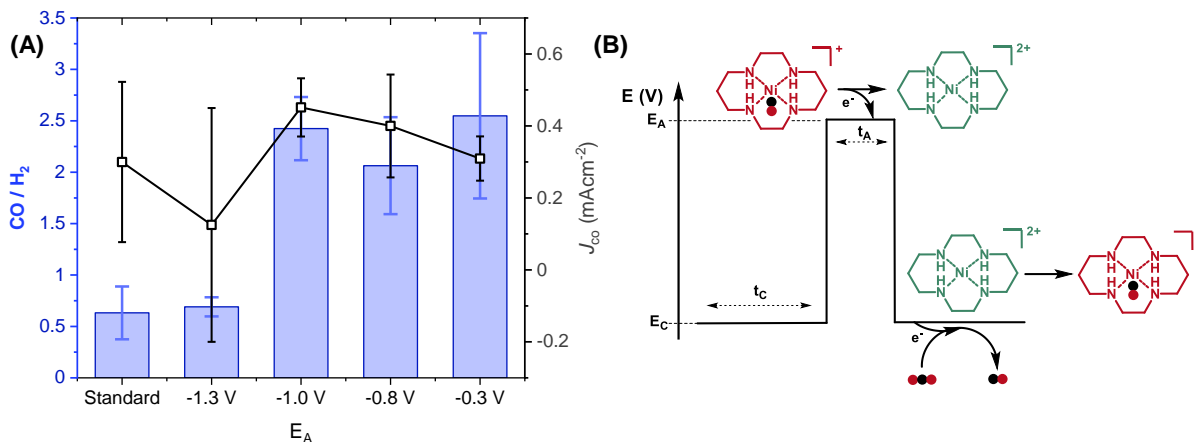


Figure 3. (A) Comparison of CO/H₂ and CO partial current densities after 3 h electrolysis of 0.1 mM $[\text{Ni}(\text{cyclam})]^{2+}$ in 0.5 M NaCl(aq) where $E_c[t_c] = -1.6 \text{ V}_{\text{Ag}/\text{AgCl}}$ [5 s]; $t_A = 0.2 \text{ s}$ with changing E_A (B) Schematic illustrating the proposed mechanism of how pulsed electrolysis can reduce catalyst degradation.

The post-electrolysis XPS analysis indicates that the prevention of $[\text{Ni}(\text{cyclam})]^{2+}$ decomposition and subsequent Ni deposition is the reason for the increased CO₂RR selectivity upon pulsing. Pulsed electrolysis may be preventing Ni deposition and preventing hydrogen evolution via both Faradaic and non-Faradaic mechanisms. We first look to non-Faradaic processes and consider if the

voltage step could be leading to a rearrangement of the electrolyte which would refresh the catalyst/CO₂ at the GCE surface and remove species such as [Ni(cyclam)(CO)]⁺, prior to their irreversible reduction. The largest rearrangement of the electrolyte would be expected to occur if the potential was stepped across the potential of zero charge (pzc) of the GCE. Differential capacitance measurements establish the pzc to be +0.4 V vs Ag/AgCl, in line with other reports (Fig S15). The pzc is significantly positive of the values of E_A (-0.3 to -1.0 V) where we see a beneficial effect of pulsing (Fig. 3 and Table S1-3).^{48,49} Some changes in the differential capacitance do occur between -0.3 and -1.0 V but it is notable that the selectivity for CO production is approximately constant when E_A is varied between these voltages (CO/H₂ ~ 2.0 to 2.5, figure 3) therefore the lack of Ni deposition and increase in selectivity for CO₂RR is unlikely to be caused by double layer rearrangement.

We next consider if a Faradaic process is occurring during pulsed electrolysis. Figure 3 shows that when E_A is positive of the oxidation of the Ni(0) species (-0.55 V Fig. 1) no increase in selectivity for CO₂RR is observed when compared to experiments with E_A at -1.0 V suggesting that Ni(0) re-oxidation is not a significant pathway. When E_A = -1.3 V the CO/H₂ drops to 0.7 ± 0.1, equal to that measured under standard electrolysis conditions. The selectivity for CO is greater for pulsed runs with E_A > -1.3V, but J_{CO} remains the same within error. This is due to an overall increase in current associated with increased hydrogen evolution when E_A = -1.3 V (or when non-pulsed conditions are used). The oxidation at -1.35 V in Fig 1 is assigned to [Ni(cyclam)(CO)]⁺ to [Ni(cyclam)]²⁺.³⁷ Therefore we conclude that pulsing decreases the concentration of [Ni(cyclam)(CO)]⁺ at the electrode surface, preventing subsequent reduction to Ni(0), Fig 3b. One past study employed a prolonged (10 minute) oxidation of a cyclam complex at very positive potentials (+0.8 V vs RHE, approximately +0.2 V vs Ag/AgCl). This led to a short-lived recovery in the rate of CO production (~ 20 minutes) but there was no significant decrease in hydrogen evolution demonstrating the importance of continuous removal of [Ni(cyclam)(CO)]⁺ using the pulsed voltage profile.³³ The sensitivity of Ni(cyclam) to short/pulsed changes in applied potential may offer insight into the wide range of selectivity's and stabilities when used in photocatalytic systems.²²⁻²⁴

Finally, we studied the time dependence of the anodic (t_A) pulse duration whilst keeping t_C constant at 5 s, Fig 4. It is desirable to minimize t_A to increase the duty cycle (percentage of time that the

device is held at operating potential). The shortest t_A value we could achieve during a prolonged electrolysis experiment with our apparatus was 40 ms corresponding to a duty cycle of >99% (Table S5). Even with this very short pulse duration we see an increase in selectivity ($\text{CO}/\text{H}_2 = 1.86 \pm 0.16$) when compared to the potentiostatic experiment. Analysis of the time-current response (Fig S8) indicates that ~ 10 ms after the start of the anodic pulse the capacitive charging current has largely decayed and that the Faradic current dominates. At 200 ms there is still a significant anodic current supporting our conclusion that the increased selectivity is the result of a Faradic process. In-line with this extending t_A to 1 s leads to a small but measurable increase in selectivity compared to when shorter pulses are used ($\text{CO}/\text{H}_2 = 3.62 \pm 0.87$, $\text{FE}_{\text{CO}} \sim 80\%$, table S2-4, Fig 4). However, it is important to note that the cathodic charge fraction (Q_C), previously proposed to be a useful parameter for assessing pulse profiles during CO_2R at metals,¹⁴ shows a large decrease when t_A 1.0 s ($Q_C = 91.2\%$, 96.3% and 97.5% for $t_A = 1.0$ s, 0.2 s and 0.04 s, table S5).

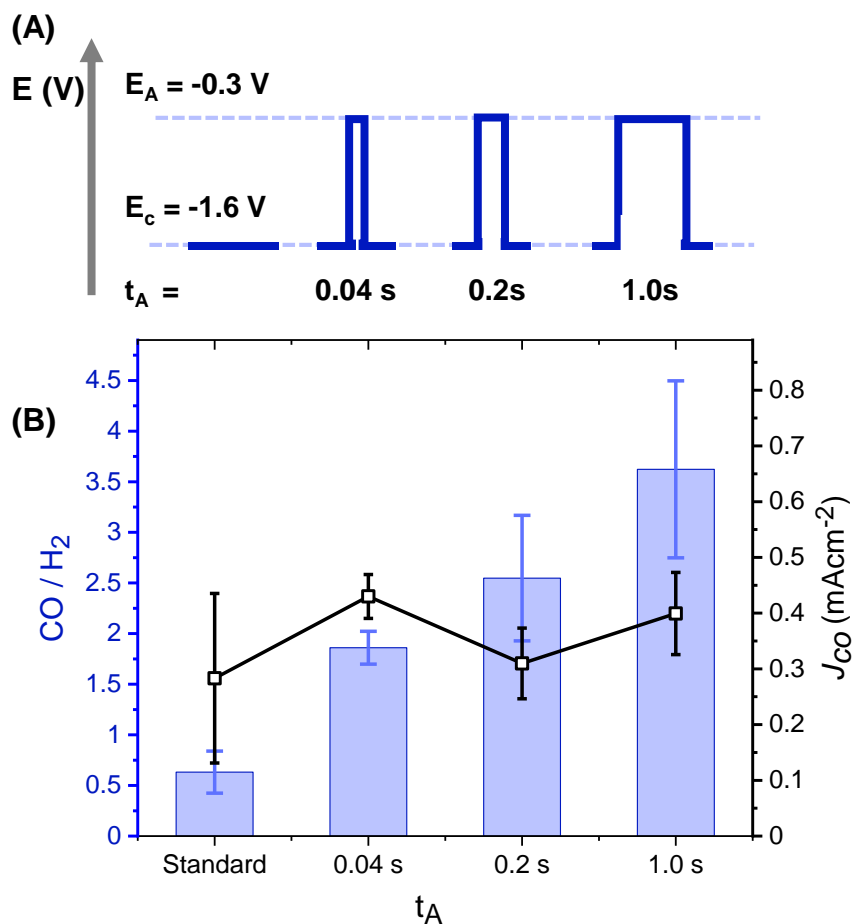


Figure 4. (A) Schematic of different pulse profiles with increasing t_a (not to scale) (B) Comparison of CO / H₂ and CO partial current densities after 3 h electrolysis of 0.1 mM [Ni(cyclam)]²⁺ in 0.5 M NaCl(aq) where $E_C[t_C] = -1.6 V_{Ag/AgCl}$ [5 s]; $E_A = -0.3 V_{Ag/AgCl}$ with changing t_A .

In conclusion here we show that short (ms - s) asymmetric voltage pulse profiles can be used to improve the selectivity and achieve stable operation of the molecular catalyst, [Ni(cyclam)]²⁺ for CO₂R to CO. We find that by rapidly removing [Ni(cyclam)(CO)]⁺, an intermediate on the pathway to an irreversible degradation product, we can achieve a CO/H₂ selectivity of > 1 for up to 12 h without the use of a CO scavenger (Fig S9). We achieve large improvements of activity with anodic pulse durations of just 40 and 200 ms corresponding to duty cycles of >99 % and 96% respectively. More widely we anticipate the use of short asymmetric pulse profiles may offer a way to modify the activity and stability of a wider range of molecular catalysts through both the in-situ regeneration of activate catalytic species and possible non-Faradic processes.

Supporting Information: Experimental methods, XPS and representative electrolysis data, and extended electrochemical characterization. All raw data is available at <https://datacat.liverpool.ac.uk/id/eprint/2272>.

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TOC Graphic: A pulsed electrolysis study on a Ni molecular electrocatalyst for CO₂ reduction shows increased CO selectivity over time, attributed to the prevention of catalyst poisoning. Investigation into the potential and time dependence of the anodic pulse gave both mechanistic insight and optimization of CO selectivity and duty cycles.

