Sustainable at both ends: electrochemical CO₂ utilization paired with electrochemical treatment of nitrogenous waste†

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We discuss the environmental and energetic benefits of coupling nitrogenous waste treatment with the electrochemical conversion of CO₂ to value-added products via direct reduction or electrocarboxylation. In particular, we demonstrate that co-electrolysis of urea or ammonia with CO₂ requires significantly lower cell voltages than CO₂ electrolysers relying on the oxygen evolution reaction as an anodic process.

The continuous growth of carbon dioxide emissions and the resulting climate change are spurring the development of technologies that convert greenhouse gases into valuable products.¹–⁴ With a noticeable decrease in the price of renewable electricity in the last decades, electrochemical solutions for CO₂ utilization are rapidly evolving.⁵–¹⁰ Electrochemical approaches include direct CO₂ reduction reactions (CO₂RRs) to single- and multi-carbon products⁵–¹⁰ and the electrochemical coupling of CO₂ to various organic precursors such as organic halides to produce carboxylic acids and esters, referred to as electrocarboxylation reactions (ECRs).¹¹–¹⁵

Despite much progress, many challenges remain for these technologies to achieve economic viability and penetrate the petrochemical market.¹⁶ One major hurdle is the high energy requirement to run the electrolyzer.¹⁷ Significant efforts are now dedicated to decreasing the voltage requirement for the cathodic process via electrocatalyst, electrolyte, and cell design.³–⁷,¹⁸ However, to decrease the overall cell voltage, more efforts need to be focused on the synergetic optimization of both anodic and cathodic processes.

The majority of reported CO₂RR systems rely on the sluggish oxygen evolution reaction (OER) as the anodic process, which requires high potentials (𝐸°OER = 1.23 V vs. RHE) and produces low-value O₂ as a product.¹⁹–²¹ In order to increase the energy efficiency of the overall cell, cathodic CO₂RR has been coupled with several alternative anodic reactions with lower energy requirements,²¹–²⁷ such as TEMPO-mediated electro-oxidation of alcohols,²³,²⁴ solar-driven oxidative dimerization of 1-phenylethanol,²⁵ electrooxidation of NaCl,²⁶ dyes,²⁷ and glycerol.²¹

Despite the advantages of all the aforementioned anodic reactions, the electrooxidation of contaminants in wastewater is an underexplored and outstanding candidate for OER replacement. Wastewater is abundant (the global production is 380 billion m³ year⁻¹) and in particular, its major nitrogenous contaminants, urea and ammonia, contain highly energetic chemical bonds.²⁸ Moreover, traditional wastewater treatment techniques are often expensive, energy intensive, and can cause secondary pollution.²⁹,³⁰ Hence, coupling anodic wastewater treatment with cathodic CO₂ utilization introduces additional value to the overall process while reducing energetic requirements.²⁷

The composition of wastewater is highly dependent on the source and may include a variety of organic compounds³¹–³⁴ making its direct electro-oxidation challenging due to the formation of toxic by-products (e.g., ClO₃⁻, NO₃⁻) and poor performance of the electrodes.²⁶,³⁵ However, the oxidation of individual components of wastewater is expected to be more controllable and selective while preventing the formation of toxic by-products. Thus, simpler wastewater mixtures from specific industries may be considered as good candidates for OER replacement.

In particular, wastewater from the massive urea production and dialysis industries are enriched in urea³⁶–³⁹ and ammonia⁴⁰,⁴¹ and may be concentrated⁴²,⁴³ for subsequent electrochemical utilization.³⁶–⁴¹ Treatment of urea and ammonia-containing effluent is essential to avoid their oxidation to hazardous nitrogen oxides in the atmosphere⁴⁴–⁴⁶ and contribution to harmful cyanobacterial blooms⁴⁷ which is exacerbated by nitrogenous waste originating from mammalian protein metabolism and agricultural runoff. Moreover, both urea and ammonia are attractive from an energetic stand-
point and have shown great potential as a fuel for fuel cells\textsuperscript{39,40} and for electrochemical hydrogen production from water.\textsuperscript{39,41} Thus, there is a strong motivation for the study of electrooxidation of urea and ammonia in combination with electrocatalytic CO$_2$ utilization.

Here, we demonstrate that the replacement of OER with ammonia or urea oxidation reactions (AOR and UOR, respectively) for electrochemical CO$_2$ utilization results in significant energy savings, while simultaneously reducing the carbon and nitrogen footprint. We consider two approaches for cathodic CO$_2$ fixation: direct reduction to CO in protic or aprotic media and ECR of organic halides in aprotic media using (1-bromoethyl)benzene (R-Br) as an organic substrate. For both approaches we show the thermodynamic requirements and experimental performance of the corresponding AOR- and UOR-based electrolyzers.

The efficiency of electrolyzers for CO$_2$ utilization directly depends on the overall cell potential, which is a sum of the standard cell potential ($E^\circ_{\text{cell}}$), the kinetic overpotentials of cathodic and anodic half-reactions ($\eta_\text{c}$ and $\eta_\text{a}$), and the ohmic drop ($E_\Omega$) arising from resistance and concentration losses (Fig. 1a, eqn (1)).\textsuperscript{48} The optimization of each parameter will significantly improve the energy efficiency of the system.\textsuperscript{48} The $E^\circ_{\text{cell}}$ is the major portion of the overall cell potential that can be calculated from the Gibbs free energy of the overall reaction (Fig. 1a, eqn (2) and (3); for calculation details, see the ESI, pages 2 and 3 Tables S1–S3).\textsuperscript{21,49} Specifically, we calculated $E^\circ_{\text{cell}}$ and $\Delta G^\circ_{\text{reac}}$ values for AOR and UOR coupled with CO$_2$RR or ECR and compared these values with those for several well-known anodic reactions, including OER, ethanol, ethylene glycol, and glycerol oxidation (Fig. 1b). OER-based electrolyzers showed the highest thermodynamic energy requirements: 257.2 kJ mol$^{-1}$ and 1.33 V for [CO$_2$RR$|$OER], and 306.5 kJ mol$^{-1}$ and 1.59 V for [ECR$|$OER]. The replacement of OER with alternative anodic reactions decreased the $\Delta G^\circ_0$ and $E^\circ_{\text{cell}}$ by 175–226 kJ mol$^{-1}$ and 0.9–1.2 V, respectively. The values obtained for UOR and AOR were comparable with that for alcohols, however, the environmental aspect made them more attractive for further investigation. Moreover, except for glycerol, the usage of alcohols for anodic oxidation is counterproductive as they are among the target products of CO$_2$RR.\textsuperscript{21,50,51}

The kinetic overpotentials for the half-reactions are the second major factor to be considered. The overpotentials depend on the mechanism of the reaction, the composition and structure of the electrocatalyst, and many other factors.\textsuperscript{52} Systematic catalyst design has helped to significantly decrease the overpotentials of cathodic and anodic reactions in the last decade (Fig. 2a, see ESI† for the full list of used references). Specifically, substantial progress has been achieved in CO$_2$RR$^5$–$^7$ and OER$^{53,54}$ in aqueous media. For instance, Au-based nanocatalysts\textsuperscript{55} showed superior activity towards CO$_2$RR to CO at $E_{\text{CO}_2\text{RR}}$ of 150 mV and strain stabilized nickel hydroxide nanoribbons decreased $\eta_{\text{OER}}$ to 162 mV.\textsuperscript{56} In contrast with OER, other anodic reactions have not been as widely investigated and consequently less attention has been devoted to their optimization. The most effective catalysts for AOR and UOR reported to date decreased the corresponding overpotentials only to about 550 mV and 1100 mV, respectively (Fig. 2b).\textsuperscript{13–38}

Based on the analysis of the reported electrocatalysts for AOR and UOR, Pt/Pt-based catalysts and Ni/Ni-based catalysts showed the best performance in AOR and UOR, respectively. Depending on the composition and the structure of the material, the reported anodic potential range was from 0.6 to 0.9 V vs. RHE for AOR (Pt) and from 1.2 to 1.5 V vs. RHE for UOR (Ni). Both ranges were lower than that for OER (from 1.4 to 1.7 V vs. RHE) (Fig. 2; for details, see ESI, Tables S5–S8†). Considering the use of state-of-the-art catalysts for these anodic reactions, the replacement of OER with UOR or AOR can decrease the cell potential by over 200 mV (Ni) and 800 mV (Pt), respectively. Thus, the minimum achievable cell potentials for aqueous CO$_2$ electrolyzers with the best reported catalysts are $\sim$0.85 V (AOR) and $\sim$1.45 V (UOR), compared to $\sim$1.65 V for the systems relying on OER.

The study of CO$_2$RRs in aprotic media drew attention due to the higher solubility of CO$_2$ in organic solvents compared to water and the complete suppression of the competing hydrogen evolution reaction (HER). However, the absence of protons in this case limits the scope of products to CO, carbonate, and oxalate.\textsuperscript{57} On the other hand, the electrochemical reduction of different organic precursors (e.g., organic halides) in aprotic media produces highly reactive species that can react with CO$_2$ at lower potentials than those required for direct CO$_2$ activation, yielding a variety of useful carboxylic acids (indirect CO$_2$RR, or ECR).\textsuperscript{11–15} These reac-

Fig. 1 Initial assessment of anodic reaction alternatives to OER. (a) Equations for the reaction energetics calculations, where $E^\circ_{\text{cell}}$ is the standard cell potential, $E_\Omega$ is the ohmic drop, $\eta$ is the sum of cathodic and anodic overpotentials, $E^\circ_{\text{red}}$ and $E^\circ_{\text{ox}}$ are the standard potentials for oxidation and reduction processes, $s$ is the stoichiometric coefficient, $\Delta G^\circ_{\text{reac}}$ is the Gibbs free energy of reaction, and $\Delta G^\circ_0$ is the Gibbs free energy of formation. (b) Energetics assessment for CO$_2$RR and ECR of RBr coupled to OER, ethanol, ethylene glycol (EG), glycerol, urea, and ammonia electrooxidation.
tions generally rely on the dissolution of sacrificial metal anodes (Mg, Al, etc.) or the oxidation of halogen-containing electrolytes.\textsuperscript{11–15} We have recently established that these processes can be replaced by environmentally friendly aqueous OER in divided systems separated by an anion exchange membrane (AEM).\textsuperscript{58} The use of AOR or UOR as the aqueous anodic process in these systems can additionally decrease the energy requirement.

To summarize and compare the potentials for CO\textsubscript{2}RR/ECR and oxidation processes (OER, AOR, UOR), we converted reported potentials to the SHE scale. The more generally used RHE scale is only applicable to reactions conducted in protic media, whereas the SHE scale can be used for both protic and aprotic electrolyte environments (Fig. 2c; for details, see the ESI, Tables S9 and 10\textsuperscript{†}). Unlike the RHE scale that considers the energy of the proton–electron couple and is only applicable for protic media, the SHE scale considers only the free energy of an electron and can thus be applied to both protic and aprotic media.\textsuperscript{5}

The analysis of the reported electrocatalysts for CO\textsubscript{2}RR (in both protic and aprotic media) and for ECR showed that the reactions in organic solvents generally proceed at more negative potentials than reactions in aqueous electrolytes. Nevertheless, significant progress in decreasing the required potentials has been achieved over the last few decades.\textsuperscript{11–15,57} In the majority of reported examples, bulk metals were used as the cathodes for ECR.\textsuperscript{11,57} Recently, nanostructured Ag showed superior performance towards ECR of α-methylbenzylbromide in acetonitrile at −1.3 V vs. SHE with nearly quantitative yield of electrocarboxylation products.\textsuperscript{58} Further minimization of overpotentials for ECR can be anticipated with advancements in nanoscale catalyst optimization.

![Fig. 2](https://example.com/figure2.png)

**Fig. 2** The potentials of selected cathodic and anodic reactions plotted in the RHE and SHE scales. The circles correspond to the onset potentials reported in literature (see Tables S5–10\textsuperscript{†} for details); the dotted lines or dashed regions correspond to $E^\circ$, with the regions in (c) arising from $E^\circ$ being pH dependent on the SHE (considered pH ranges are shown in brackets). (a) The half-reactions for ECR and CO\textsubscript{2}RR in aprotic media (green background), CO\textsubscript{2}RR, OER, AOR and UOR in protic media (blue background). (b) Examples of cathodic reactions (CO\textsubscript{2}RR to CO), and anodic reactions (OER, AOR, and UOR) performed in aqueous media at different electrocatalysts with the corresponding potentials plotted on the RHE scale. (c) Examples of cathodic reactions (CO\textsubscript{2}RR to CO, ECR), and anodic reactions (OER, AOR, and UOR) performed in protic and aprotic media at different electrocatalysts with corresponding $E^\circ$ plotted on the SHE scale. The onset potentials and $E^\circ$ ranges are shown for the optimal pH ranges for each reaction ($E^\circ_{\text{CO}_2/\text{CO}}$ in protic at pH = 0 is shown for reference only); in the aprotic medium, $E^\circ_{\text{CO}_2/\text{CO}}$ range arises from the variation in trace water content in the electrolyte. The dotted line for $E^\circ_{\text{R}_+/\text{R}^-}$ corresponds to the thermodynamic potential required to form α-methylbenzyl anion (ECR).
Standard reaction potentials ($E^0$) were used to assess the thermodynamic limits for catalyst improvement (Fig. 2c). The $E^0$ of CO$_2$RR to CO in aprotic electrolytes depends on the water content, resulting in potentials ranging from $-0.8$ V to $-1.1$ V vs. SHE.\textsuperscript{59} In addition to a similar “wet” solvent effect, the $E^0$ of ECR of organohalides is strongly dependent on the structure of the initial halide and can vary in a wide range.\textsuperscript{60} The benzyl halide used in this work has $E^0 \approx -0.8$ V vs. SHE.\textsuperscript{61}

For all the reactions in protic media, the $E^0$ on the SHE scale is a function of the electrolyte pH. Specifically, in the case of aqueous CO$_2$RR to CO, the $E^0$ range from $-0.9$ V to $-0.5$ V vs. SHE as the reported pH values of catholytes varied from neutral to highly alkaline.\textsuperscript{62,63}

For the anodic reactions (AOR, UOR, OER), the $E^0$ were within a 59 mV range due to only small pH variations for the reported systems.\textsuperscript{36–41} The potential ranges arising from conversion to the SHE scale (see page 4 in ES1), especially for organic media, make the estimation of the overpotentials difficult. Thus, the use of individual electrode potentials along with the overall cell voltages instead of the overpotentials is more suitable for describing electrochemical reactions in divided cells with two different electrolytes in cathodic and anodic compartments, especially for organic–aqueous systems.

To assess the feasibility of combining AOR or UOR with each of the aforementioned CO$_2$ electrotreatment processes (i.e., CO$_2$RR in aqueous and aprotic media, and ECR in aprotic medium), we performed experimental electroanalytical evaluations of their combinations. Coupled electrolysis was performed in a two-compartment H-cell divided by an AEM. The anodic oxidation of ammonia and urea was performed in a 5 M KOH anolyte at commercially available anodes: Ni foam for urea and Pt mesh or Pt/C for ammonia. The cathodic CO$_2$RR and ECR in aprotic media were performed at a carbon-clath-supported Ag nanoparticle cathode with 0.1 M tetrabutylammonium bromide in acetonitrile as catholyte. CO$_2$RR in an aqueous catholyte (5 M KOH) was performed using a flow reactor with a gas diffusion electrode (GDE) to ensure high access of CO$_2$ to the reactive surface of the cathode.\textsuperscript{62} We note that we did not perform ECR in a GDE-based flow cell, as hydrophobic GDEs are designed to work with aqueous electrolytes and fail in organic medium due to fast flooding.\textsuperscript{64}

First, linear sweep voltammetry (LSV) was performed for the selected cathodic and anodic processes (Fig. 3). In agreement with previous reports,\textsuperscript{38,63} the onset potential of CO$_2$RR at 10 mA cm$^{-2}$ was $-1.3$ V vs. SHE in both protic and aprotic media. However, the aqueous CO$_2$RR in the GDE/flow cell setup showed significantly higher current densities than that in the aprotic medium at the same potential, as the latter was conducted in the H-cell with associated mass transport limitations.\textsuperscript{63} For the ECR performed in the H-cell, the reduction of the organic bromide (RBr) occurred at lower potential than that required for direct CO$_2$RR. At $-0.6$ V vs. SHE, RBr undergoes its first electron transfer to produce the corresponding free radical R’, that is inactive towards CO$_2$. At the more negative potentials than $-0.9$ V vs. SHE, R’ undergoes a second electron transfer to produce R$^-$ followed by its reaction with CO$_2$, yielding the target electrocarboxylation products (carboxylic acid and ester).\textsuperscript{58} Thus, the indirect reduction of CO$_2$ requires a significantly lower energy input compared to the direct electroreduction of CO$_2$ ($\Delta E \approx 400$ mV).

Since AOR was observed at significantly lower potentials than UOR and OER, the performance of a [CO$_2$RR|AOR] electrolyzer was investigated first (Fig. 4). The cell performance was characterized by measuring the individual electrode potentials at current densities ranging from 100 $\mu$A cm$^{-2}$ to 10 mA cm$^{-2}$ using chronopotentiometry (CP). The anodic potential (Fig. 4b, inset) and the overall cell potential (Fig. 4b) were low only at very low current density (0.5 mA cm$^{-2}$) and rose rapidly with its increase (see also Fig. S1†). Moreover, a durability test showed a significant drop in the activity of the Pt anode towards AOR after each hour of operation due to the poisoning of the surface by N$_{ads}$ intermediates, such as NH$_{ads}$ and N$_2$H$_{y,ads}$.\textsuperscript{66–69} After 4 hours of operation, the Pt
catalyst lost activity towards AOR, with its $E-J$ trace matching that for OER-only operation (Fig. 4b). The fast poisoning of the catalyst surface (similar to earlier observations in the literature)\textsuperscript{70–75} and small current densities limit the practicality of AOR and indicate the need to develop more durable electrocatalysts with weaker M–N\textsubscript{ads} bond strength to decrease surface poisoning and facilitate AOR.

In contrast, UOR-coupled CO\textsubscript{2} electrolysis showed good stability in the anodic performance (no change for over 4 hours). A stable potential was observed at all studied current densities, specifically, 5–80 mA cm\textsuperscript{-2} in the aprotic H-cell experiments and 5–100 mA cm\textsuperscript{-2} in the aqueous flow cell experiments (Fig. 5 and S2†). In all these cases, the operating cell potential decreased by 0.2 V in comparison with electrolyzers having OER as the anodic reaction (Fig. S3†).

The cell voltage trends in Fig. 5e not only clearly show the impact of the anodic reaction substitution, but also enable us to compare the overall $E_{\text{cell}}$ with the cathodic reactions performed in both protic and aprotic environments. While coupling aqueous CO\textsubscript{2}RR with UOR instead of OER brought the $E_{\text{cell}}$ down by 0.2 V, simultaneous switching of the cathodic environment from aqueous (CO\textsubscript{2}RR\textsubscript{aq}) to aprotic (CO\textsubscript{2}RR\textsubscript{org}) decreased $E_{\text{cell}}$ by up to additional 0.2 V. The same CO\textsubscript{2}RR product (CO) was produced in both configurations. The $J-E_{\text{cell}}$ line was less steep in the case of the CO\textsubscript{2}RR\textsubscript{org} because of the more pronounced mass transport limitations of the H-cell electrolyzer, compared to the GDE-based flow setup in which CO\textsubscript{2}RR\textsubscript{aq} was performed. Compared to the direct CO\textsubscript{2}RR\textsubscript{org} ECR (i.e., electrochemical activation of R–Br followed by the reaction with CO\textsubscript{2}) decreased the cathodic voltage requirement by up to additional 0.8 V. While in this case CO\textsubscript{2} was converted to the carboxylate RCO\textsubscript{2}– (ECR), as opposed to CO (CO\textsubscript{2}RR\textsubscript{org}), this approach resulted in the total $E_{\text{cell}}$ improvement in the aprotic CO\textsubscript{2} electrolyzer of up to 1 V in a wide range of operating current densities (Fig. S3a†). The examined CO\textsubscript{2} electrolyzers performed with high faradaic efficiencies (FE) of target products when using UOR as the anodic process. Both [CO\textsubscript{2}RR\textsubscript{aq} UOR] and [CO\textsubscript{2}RR\textsubscript{org} UOR] systems performed with FE\textsubscript{CO} of up to 90% and 93% at the cathodic side, respectively, which is consistent with the previous reports on CO\textsubscript{2}RR at Ag nanoparticle cathodes in aqueous\textsuperscript{65} and aprotic\textsuperscript{58} environment (Table S15†). Specifically, for aqueous systems, minor HER is inevitable even when a GDE-based three-phase interface is present.\textsuperscript{65} In acetonitrile, minor HER occurs due to the traces of water in acetonitrile used without prior drying as well as the possibility of minor crossover of water from the aqueous half-cell.\textsuperscript{58} The potentiostatic cathodic ECR also showed high yields of carboxylation products, i.e., RCO\textsubscript{2}H and RCO\textsubscript{2}R, of up to 90%, in agreement with the previous report\textsuperscript{58} (Table S15†).

![Fig. 5 The schematics and performance of [CO\textsubscript{2}RR]\textsubscript{aq}|UOR and [ECR|UOR) electrolyzers. (a) An H-cell used for organic [CO\textsubscript{2}RR]\textsubscript{aq}|UOR or [ECR|UOR) co-electrolysis. (b) A flow reactor used for aqueous [CO\textsubscript{2}RR]\textsubscript{aq}|UOR co-electrolysis. (c and d) The individual electrode potentials as a function of the total current density for the H-cell (c) and flow (d) electrolyzers. (e) The total current density as a function of the cell potential for the H-cell and flow electrolyzers.](image)

Conclusions

In conclusion, we demonstrated that the replacement of OER with ammonia or urea oxidation reactions in electrochemical systems for CO\textsubscript{2} utilization results in significant energy savings and simultaneous carbon and nitrogen footprint mitigation. Despite the very low standard potential of AOR, the process at current Pt-based electrocatalysts proceeds with fast catalyst poisoning by N\textsubscript{ads} intermediates and cannot be used for efficient CO\textsubscript{2}-electrolyzers. Thus, more durable electrocatalysts with weaker M–N\textsubscript{ads} bond strength need to be developed. The replacement of OER with UOR decreased the overall cell potential by up to 210 mV. In the case of CO\textsubscript{2}RR conducted in an aprotic medium with UOR as the anodic process, a simultaneous replacement of CO\textsubscript{2}RR by the ECR of (1-bromoethyl) benzene resulted in a total cell voltage improvement of up to 1 V in a wide range of operating current densities and with a high yield of electrocarboxylation products. The performance and energy requirements of the overall cell will continue to improve with further development of ammonia and urea electrooxidation catalysts. This approach brings CO\textsubscript{2} electrolyzers one step closer to industrial implementation by demonstrating how a judicious choice of paired reactions can significantly minimize CO\textsubscript{2} electrolyzer energy requirements while provid-
ing additional economic and environmental value through urea and ammonia waste treatment.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the University of Waterloo (Startup and Trailblazer Funding), Waterloo Institute for Nanotechnology (WIN-MESA + Seed Funding), Science and Engineering Research Council of Canada, Canadian Foundation for Innovation, and Ontario Research Fund for the financial support of this work. We also thank Kieran Schmidt for preparing the TOC artwork and Helen Engelhardt for formatting the ESI.†

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Communication

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