

Review Article

The rebirth of urea oxidation reaction for power-to-X and beyond

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Abstract

Despite the longstanding interest in urea oxidation reaction (UOR), the identification of reaction products under conventional conditions was only reported recently. It turns out that the initially thought “sustainable pathway”, leading to harmless products, represents just a small fraction of the overall reaction mechanism. This is detrimental as the use of urea-rich aqueous feeds for H₂ production, along with their remediation through UOR, constitutes perhaps the most important added value of this process for power-to-X and clinical applications. Nonetheless, promising strategies favoring the formation of environmentally friendly products over harmful overoxidized ones already exist. This is expected to lead to a “rebirth” of this research field and open the quest for ultimate selectivity to ensure the complete sustainability of UOR. Therefore, the systematic analysis of reaction products, the elucidation of mechanisms for improving N₂ faradaic efficiency, and the design of selective catalysts should be the next focus of research in the field of UOR.

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Keywords

Urea oxidation reaction, Power-to-X, Remediation, Artificial kidneys, Nitrites.

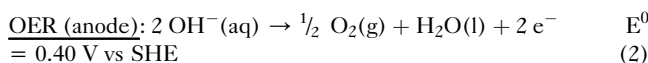
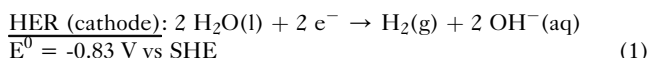
Abbreviations

EC, electrochemical-chemical; HER, hydrogen evolution reaction; LED, light-emitting diode; OER, oxygen evolution reaction; PEC, photo-electrochemical; RHE, reversible hydrogen electrode; SHE, standard hydrogen electrode; UOR, urea oxidation reaction; UV, ultraviolet.

UOR: background

Urea, CO(NH₂)₂, is a naturally occurring molecule found in the urine of mammals, as well as in some plants and bacteria. It is also a commodity chemical widely employed in the fertilizer, animal feed and chemical industry [1]. Daily, humans and animals excrete millions of tons of urine, containing mainly water and urea. Although urea can be used as a fertilizer, untreated urea-containing wastewater can pose severe environmental threats such as eutrophication or acid rain. Currently, various methods are used to purify urea-containing wastewater and electrochemical treatments of urea-rich effluents are interesting for metropolitan wastewater management organizations [2]. The electrochemical oxidation reaction of urea (UOR) is an electrochemical process that has the potential to play a crucial role in clean energy technologies. It provides a promising solution for generating hydrogen (H₂), to be stored and used as an energy carrier while simultaneously purifying urea-rich waste waters (Fig. 1a). Such processes could be, in principle, adapted with wastewater enriched in urea from large-scale industrial or animals breeding facilities.

In traditional alkaline water electrolysis, the cathodic hydrogen evolution reaction (HER, **Reaction (1)**) and the anodic oxygen evolution reaction (OER, **Reaction (2)**) occur at a theoretical cell potential of 1.23 V.



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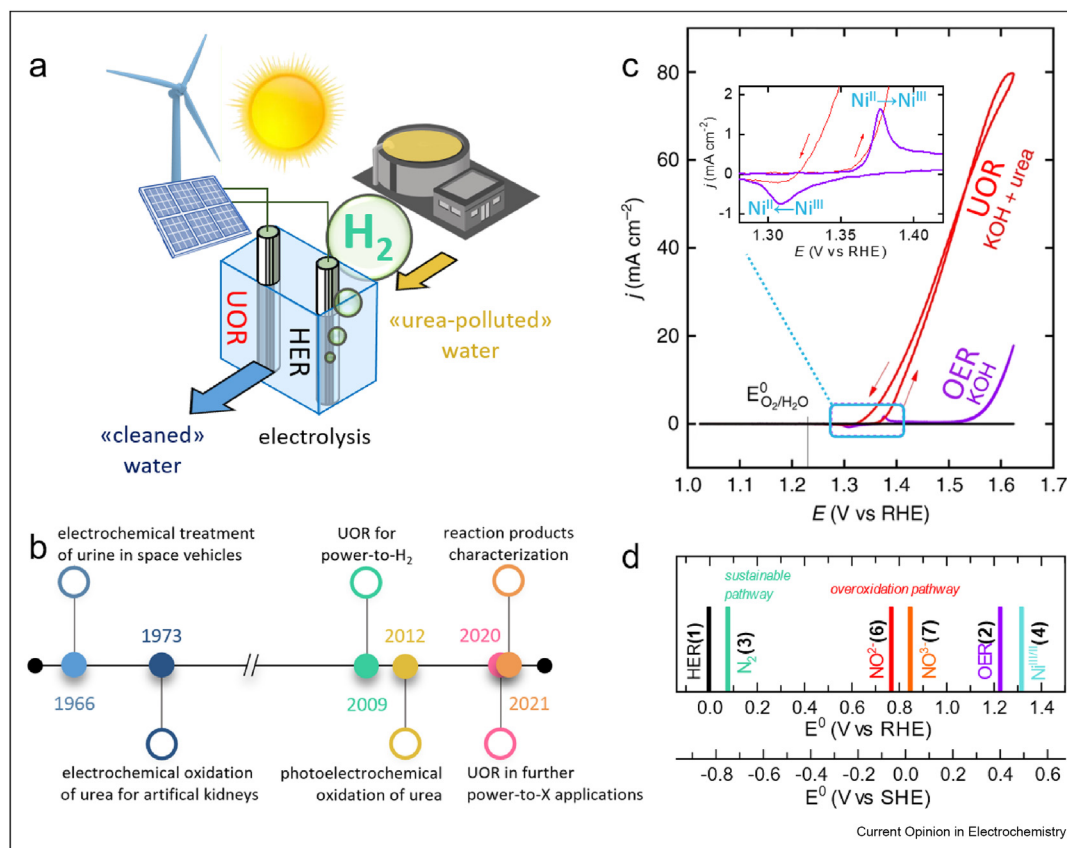
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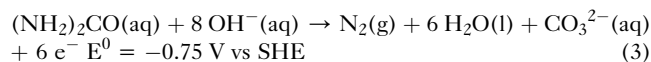
Figure 1



a) Scheme depicting the use of UOR in an electrolysis setup for power-to-H₂ coupled to water remediation. **b)** Chronological chart showing UOR milestones. **c)** Cyclic voltammograms obtained with a Ni-based anode, in 1 M KOH (purple curve) and 1 M KOH + 0.33 M urea (red curve). The standard potential of O₂/H₂O is shown by a black vertical line, the Ni^{III}/Ni^{II} redox peaks are indicated by a blue box, the arrows indicate the sweep direction. The inset shows the Ni quasi-reversible redox system. Adapted with permission from Ref. [13]. **d)** Plot showing the E⁰ values for the main reactions presented in this article (at pH = 14), the numbers in brackets refer to the reaction numbers in this article.

UOR, which is a different anodic process, can be considered as a replacement for OER. Surprisingly, since the beginning of the research on UOR for energy conversion [3], only **Reaction (3)** (referred here to as the “sustainable pathway”) was considered for that process.

UOR “sustainable pathway” (anode):



Considering its low standard potential [3–6], employing UOR instead of OER at the anode allows for a considerable decrease in the input energy of the cell, with a theoretical cell potential of 0.07 V when UOR is coupled to HER (**Reactions (1,3)**) vs 1.23 V for water electrolysis (**Reactions (1,2)**) [5]. However, despite its low thermodynamic requirement, the UOR is a complex

multielectronic process that requires the use of efficient electrocatalysts (most of the time, based on Ni). Therefore, to occur, it requires the application of a considerable overpotential, and, in practice, the application of a cell potential higher than 1.3 V is required to trigger HER and UOR simultaneously, which is still lower than that required for water electrolysis (1.5–1.6 V). Besides such thermodynamic considerations, the possibility of using UOR to produce H₂ from urea-rich aqueous feedstocks is highly attractive in the current context of dwindling drinking water resources [7].

Besides its promise for power-to-H₂, water remediation, clinical, and sensing applications (briefly presented in Section [Unconventional applications of UOR: promises and expectation](#)) UOR is a key reaction in urea fuel cells [8] and urea has also been considered as a hydrogen carrier [1]. However, these aspects will not be described

in this review. Several milestones in UOR research [3,4,7,9–12] are summarized in chronological order in Fig. 1b. In addition, the “conventional” UOR experimental conditions used in most power-to-H₂ reports, established from the pioneering work of Botte *et al.*, are listed in Table 1.

Recently, several noteworthy papers discussing UOR mechanisms variants or reviewing UOR electrocatalysts have been published [14–20]. However, in light of the most recent reports on additional (overoxidized) product identification, and corresponding refined intra- and intermolecular reaction mechanisms [4,5], an updated perspective on UOR is required to facilitate further high-standard research in this rapidly evolving field.

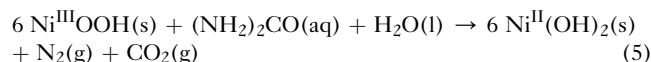
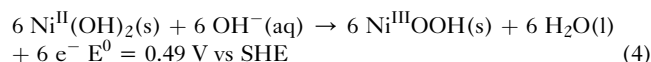
Reaction products and mechanisms

Initially identified catalytic active species, products, and bottlenecks

An important aspect of UOR is that it typically occurs in conditions very favorable for OER (high pH, Ni-based electrodes, and high potentials). Looking at the voltammograms of Fig. 1c, it seems obvious that OER can compete with UOR if too high potentials are applied to the anode (in this case when $E > 1.5$ V vs RHE). Indeed, O₂ is frequently detected as an UOR byproduct [21]. If needed, this competition can be avoided by operating a sufficiently low potential, below the OER onset. This can be, however, a practical problem, when high current densities are required. Recently, a NiS₂-based catalyst has been found to inhibit undesired OER in the presence of urea at high overpotential (>1.6 V vs RHE), allowing to reach a current density in the order of 300 mA cm⁻² with almost no O₂ produced [22]. UOR electrocatalysts are usually based on Ni, therefore, most mechanistic studies have been performed with Ni(OH)₂, the phase likely generated at the outermost part of Ni-based catalysts in highly alkaline electrolytes. An UOR feature, that can be directly observed on voltammograms, is that the reaction onset is localized at the same potential as that of the quasi-reversible oxidation wave corresponding to the conversion of Ni^{II}(OH)₂ to Ni^{III}OOH (blue box and inset in Fig. 1c) [13]. This shows that UOR onset is related to the formation of Ni^{III} species onto the catalyst layer. Indeed, it is broadly admitted that UOR occurs through an electrochemical-chemical (EC) mechanism, where

electrochemically generated Ni^{III}OOH (**Reaction (4)**) chemically reacts with urea and regenerates Ni(OH)₂ (**Reaction (5)**). The corresponding ideal 6 e⁻ “sustainable” UOR mechanism (overall **Reaction (3)**) is usually expressed as follows:

Electrochemical-chemical (EC) mechanism of the UOR “sustainable pathway” (anode):



Note that in **Reaction (5)** CO₂ is denoted as a gaseous product but at that pH it is solubilized in a carbonate form, as shown in **Reaction (3)**. The existence of the EC catalytic loop involving Ni^{II} and Ni^{III} species has been demonstrated since the early days of UOR using *operando* spectroscopy [23] and electroanalytical techniques [24,25]. In an attempt to get more insight into this mechanism and explain the widely admitted (but overlooked) selective N₂ formation through UOR, several recent publications have reported detailed mechanisms and proposed UOR active species [19,26,27]. However, these mechanisms should be reconsidered in light of current knowledge about the products of the UOR reaction, described in the next paragraph [4,5]. Another aspect of UOR that has been a serious bottleneck is the considerable drop in activity occurring during the reaction. Although the reason for this is still unclear, one can expect that it originates from complex mass-transport effects, competition with other reactions, or passivation of active sites by reaction products. However, recently developed UOR catalysts derived from NiMoO₄ [28] or Ni₂Fe(CN)₆ [29] seem to overcome this limitation as they allowed performing UOR at high current densities for several days.

Newly identified reaction products

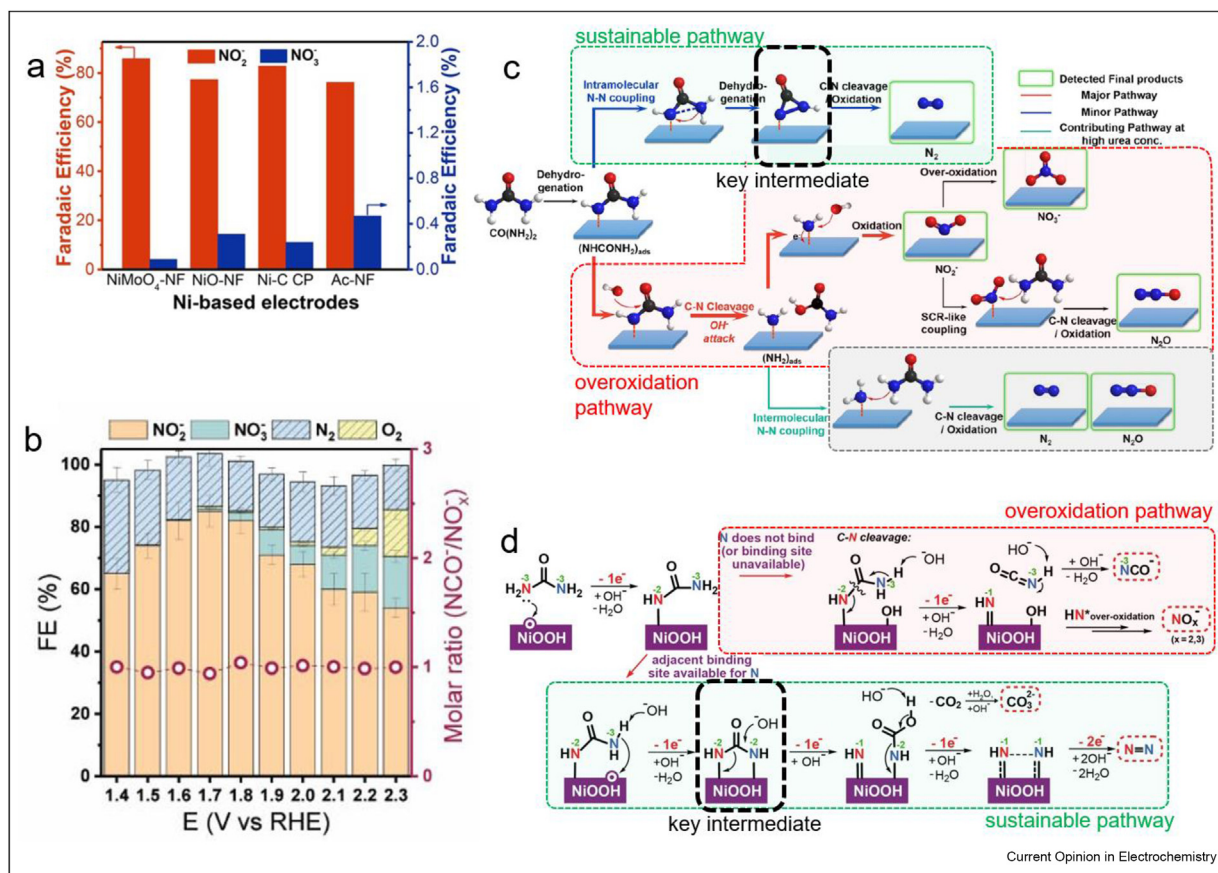
Surprisingly enough, since the first report on UOR for energy conversion [7], the only route that was considered was the 6 e⁻ pathway leading to selective N₂ formation (**Reaction (3)**). This consideration made UOR particularly appealing for power-to-H₂ coupled with water remediation, as it was expected to produce only

Table 1

Conditions employed in the majority of UOR papers on power-to-H₂ using a conventional three-electrode cell setup at 25 °C.

Electrolyte composition	Electrolyte pH	Electrocatalysts	Range of onset potential
0.33 M urea + KOH in water	~14	Ni-based	1.3–1.4 V vs RHE 0.45–0.55 V vs SHE

Figure 2



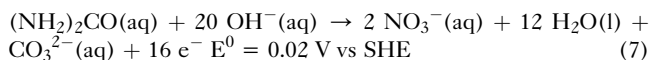
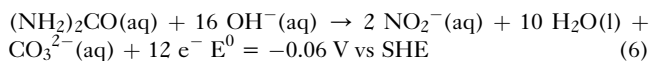
a NO_2^- and NO_3^- Faradaic efficiencies for several Ni-based electrocatalysts in 1 M KOH + 0.33 M urea. **b** Faradaic efficiencies of major products for a $\text{Ni}(\text{OH})_2$ -modified Ni foam during 1 h electrolysis in 1 M KOH + 0.33 M urea. **c** UOR pathway proposed by Li et al. Adapted with permission from Ref. [4]. **d** UOR pathway proposed by Tatarchuk et al. Adapted with permission from Ref. [5]. In panels c) and d), the UOR “sustainable pathways”, the “overoxidation pathways”, and the proposed key intermediates for sustainable pathways are indicated by green, red, and black boxes, respectively.

harmless compounds (N_2 and CO_3^{2-}). Two recent breakthrough reports strongly contradicted this assumption. In 2021, analysis of the electrolysis products at a series of Ni-based electrocatalysts (Ni, NiO, NiMoO_4 , and activated Ni), studied at different potentials in conventional UOR conditions (Table 1), revealed the main oxidation product to be, by far, nitrites (NO_2^-), with a corresponding Faradaic efficiency of $\sim 80\%$ (Fig. 2a) [4]. The authors of this study showed that small amounts of NO_3^- and N_2O were also produced and that the amount of N_2 was minimal, with a corresponding Faradaic efficiency of only $\sim 20\%$. In 2022, another important report confirmed these findings and revealed the concomitant formation of NCO^- , a well-known poison, at quasi-stoichiometric quantities with respect to NO_2^- and NO_3^- (i.e., NO_x^- , Fig. 2b) [5]. According to the authors, NCO^- results from urea degradation during UOR. These results have been seriously considered by some authors and, since then, analysis of the electrolysis products has been performed

in several studies, confirming the formation of NO_2^- [22,25,30,31]. It is also worth noting that the formation of ammonia as a major product was identified at Ni-based electrodes in a recent paper [25], highlighting that efforts are still required for clarifying reaction products. On one hand, some authors have claimed that the formation of NO_2^- can be beneficial for the synthesis of added-value chemicals [31]. On the other hand, the formation of NO_x^- , and particularly NO_2^- , can be seen as problematic because this compound is classified as a possible carcinogen (group 2A of by the International Agency for Research on Cancer). This generates doubts about the potential use of sustainable UOR for wastewater remediation in most reported conditions. Overall, these important recent results demonstrate that: overoxidation of nitrogen compounds occurs in conventional UOR conditions, UOR is more complex than the initially presumed 6 e^- pathway (Reaction (3)), and UOR in conventional alkaline conditions yields harmful NO_x^- (and NCO^-) compounds.

The reactions involving the formation of NO_x^- , referred here to as the “overoxidation pathway” are presented below [4]. The standard potentials (E^0) were calculated based on that reported by Tatarchuk *et al.* [5] and are plotted along with those of **Reactions (1–4)**, in **Fig. 1d**.

UOR “overoxidation pathway” (anode):



Proposed mechanisms

The two previously presented reports brought to light the formation of overoxidized reaction products and provided a basis for mechanism elucidation. By using isotopically labeled NO_2^- and urea, Li *et al.* found that: *i*) N_2 is not a downstream product of NO_2^- , *ii*) N_2O originates from NO_2^- , *iii*) the major pathway for N_2O formation is intermolecular, and *iv*) N_2 formation occurs through intramolecular and intermolecular pathways [4]. According to these results and additional electrolysis performed with urea analogs, they proposed the mechanism shown in **Fig. 2c**. Here, N_2 formation occurs through two routes. The first pathway, referred to here as the “sustainable pathway” (not involving the formation of harmful substances, green boxes in **Fig. 2c** and **d**) is an intramolecular process leading to N_2 . The second pathway for N_2 formation is an intermolecular process whose contribution depends on the urea concentration (grey box in **Fig. 2c**). The last and the main pathway, referred to here as the “overoxidation pathway” (involving the formation of harmful substances, red boxes in **Fig. 2c** and **d**) leads to NO_2^- formation, and is, by far, the major contributor in UOR. It occurs through the cleavage of the C–N bond and oxidation of adsorbed NH_2 species. NO_3^- and N_2O species are products originating from NO_2^- [4]. Tatarchuk *et al.* proposed alternative mechanistic UOR pathways in line with the formation of NCO^- , shown in **Fig. 2d** [5]. While these two reports converge on many aspects, they also diverge in an insightful and complementary manner. A notable difference, concerning the intramolecular “sustainable pathway” is that, for the first group, the key intermediate involves the formation of a constrained triangular cyclic species with a single coordination point on the electrode surface [4] while, for the second group, it rather involves the bonding of both urea nitrogen atoms to adjacent surface sites (black boxes in **Fig. 2c** and **d**) [5].

Toward the UOR “sustainable pathway”: improving selectivity

Li *et al.* and Tatarchuk *et al.* not only reported on product formation and mechanisms, but they also provided

strategies for favoring the “sustainable pathway” and increasing the UOR selectivity toward N_2 formation. It was first found that coating the Ni catalyst with polyaniline increases the N_2 Faradaic efficiency by a factor of two [4]. This effect was ascribed to a locally increased urea concentration caused by supramolecular bonding, a change in surface wettability effect, or a redox shuttle effect [4]. Afterward, the doping of the Ni-based anode by Cu atoms was found to considerably increase the Faradaic efficiency of N_2 production, by lowering the energies of key intermediates (according to density functional theory calculations) [5]. By combining the two approaches, Faradaic efficiencies up to 65% for N_2 formation were reached [5]. These considerable improvements are extremely promising for future research on UOR and the mechanisms favoring the “sustainable pathway” require further understanding for ultimately suppressing the “overoxidation pathway”.

Unconventional applications of UOR: promises and expectation

Sun-to- H_2

A direct sun-to- H_2 conversion route consists of using photoelectrochemical (PEC) cells. Typically, in these systems, electron–hole pairs (e^- - h^+) photogenerated in a semiconductor electrode (i.e., a photoelectrode) react with water (HER and OER, **Reactions (1,2)**) at the solid/liquid interface. Key challenges in this field of research are: improving the stability of immersed semiconductors, enhancing reaction kinetics at semiconductor surfaces, and reaching a high photovoltage with cost-relevant materials to trigger the energy-demanding water-splitting half-reactions [32]. Naturally, UOR seems an anodic process of choice for decreasing photovoltage requirements and for increasing photocurrent densities at low overpotential. In addition, PEC cells may also be compatible with urea-containing wastewater as a feed. This approach has now been assessed by several groups [11,13,30,33–41]. In the first report, $\text{Ni}(\text{OH})_2$ -modified TiO_2 and α - Fe_2O_3 nanowires photoanodes were tested and stable photocurrents were reported in a standard UOR electrolyte (**Table 1**) and with urine [11]. The improvement of photoelectrochemical performance by $\text{Ni}(\text{OH})_2$ was then further confirmed on Ti-doped α - Fe_2O_3 [30,35]. Besides, BiVO_4 , a semiconductor widely used for OER photoanodes, modified with a Co-based coating [38] or co-modified with Co- and Ni-based coatings [39] was investigated as a UOR photoanode in neutral pH electrolyte.

Si is a particularly relevant candidate to be used as a photoelectrode substrate [40] and several Si-based photoanodes were tested for UOR. Modification of Si photoanodes with $\text{Ni}(\text{OH})_2$ catalytic coatings generated *in situ* from various Prussian-blue derivatives [13,41] or directly deposited [33] was found to considerably improve the PEC performance for UOR, however, these

strategies led to limited stability in operation at low potentials (i.e., at which OER is not competitively occurring, Section [Initially identified catalytic active species, products, and bottlenecks](#)). Conversely, the modification of Si-based electrodes with amorphous Ni–Mo–O coatings led to considerable improvement in operation time at a low potential [34]. The first report on the analysis of PEC UOR reaction products was only published in 2023. Specifically, very low Faradaic yields for N₂ production (10–18%) and significant formation of NO₂[−] were reported [30], well in line with recent reports on more conventional electrodes (Section [Newly identified reaction products](#)).

Beyond power-to-H₂

As an alternative to OER, UOR can also be beneficial for other power-to-X processes. This is the case, for instance, in power-to-chemical processes involving electrochemical CO₂ reduction. The use of UOR in conventional conditions (Table 1) for improving two different CO₂ membrane electrolyzers containing Ag-based cathodes (known to selectively produce CO) has been proposed [3]. First, in a CO-producing electrolyzer comprising a gas diffusion cathode, the use of UOR (at modified Ni foam anodes) led to a performance increase and a stable operation for 2.7 h [42]. Second, it was reported that the presence of urea in a formate-producing membrane electrolyzer (comprising a Sn cathode in a NaHCO₃ catholyte and NiFe anode in a 1 M NaOH anolyte) did not affect the formate Faradaic efficiency [43]. UOR was also considered for power-to-NH₃. In particular, UOR considerably increases anode performance (in this case, a Ni foam modified with carbon and Cu oxides) in Na₂SO₄ electrolytes. Coupling these UOR anodes with an N₂-reduction cathode of the same material allowed reaching a Faradaic efficiency of 23.9% for NH₃ synthesis [12]. If these reports present UOR as an attractive alternative to OER for CO₂ and N₂ reduction, so far, no interest was given to the anodic reaction products as UOR was assumed selective towards N₂ and CO₃^{2−} formation (**Reaction (3)**).

Clinical applications of UOR: artificial kidneys

As described in Section [UOR: background](#), research on electrochemical urea oxidation started in physiological conditions. Even if this medium is very different from the conventional UOR electrolytes used for power-to-H₂ (Table 1), it seems useful to briefly discuss the evolution of this field which has a long history. Urea removal in dialysates has been identified for decades as an important step toward the design of portable dialysis units such as artificial kidneys. In this frame, the interest in the electrochemical removal of urea started in the early seventies, with a paper reporting the electrochemical oxidation of urea at Pt electrodes in physiological conditions, proposing CO₂, N₂, and H₂O as final products [10]. For clinical applications, the presence of

chloride in dialysates is an additional important parameter as the oxidation of Cl[−] to Cl₂ is likely to occur simultaneously with urea oxidation, leading to reactive species, which can be beneficial for urea degradation but may also be detrimental by generating additional hazardous species. Although the first reports seemed promising, so far, electrochemical degradation of urea has not been applied in practice for clinical applications. According to some authors [44,45], this is likely caused by: *i*) the absence of a clear electrochemical response of urea in physiological media, *ii*) leaching from the electrode, *iii*) acidosis, and *iv*) formation of hazardous species such as nitrite, nitrates, ammonia, chloramines, and oxidized glucose species. Interestingly enough, PEC urea oxidation (see Section [Sun-to-H₂](#)) has been recently considered for dialysate regeneration in wearable artificial kidneys. TiO₂ [46] or Fe₂O₃ [47] nanowires photoanodes illuminated with UV light-emitting diodes (LEDs) were recently identified as potential candidates for the decomposition of urea at a therapeutic rate. The possibility of harmful side-product generation has been identified for a long time for biomedical UOR applications. This consideration is still seriously taken into account for artificial kidneys, and membranes are considered for separating the dialysate loop from the urea oxidation circuit [48]. Nevertheless, recent research progress on UOR for power-to-H₂ (see Section [Reaction products and mechanisms](#)) will probably bring a new look into this field and may accelerate developments for clinical technologies.

Sensing applications of UOR

Monitoring urea concentration is important for manufacturing processes, environmental protection, and clinical analysis. Ureases are widely utilized for urea sensing due to their exceptional catalytic activity and binding capabilities, they are, however, subject to denaturation. Therefore, general interest is also given to non-enzymatic detection methods, presumably more robust. An indisputable effect of the UOR is that it produces a considerable anodic catalytic current in appropriate conditions (Fig. 1c). This current depends on urea concentration [49] and can therefore be employed for the determination of urea concentration. So far, many anodes containing Ni compounds such as Ni oxide, Ni sulfides, Ni-containing high entropy alloys, and Ni metal–organic frameworks, sometimes mixed with conductive materials like graphene or pyrolyzed carbon have been employed for urea detection using UOR. Many of the classical electroanalytical methods have been employed for urea sensing in alkaline UOR conditions [50–54]. It is also worth mentioning that a few studies successfully employed lower pH electrolytes (pH 8 or 6) [55,56]. In general, such UOR-active anodes exhibit a limit of detection in the range of 1–20 μM and several authors tested them with water or urine samples [52,57]. Alternatively, PEC detection with Si-based photoanodes (see

Section [Sun-to-H₂](#)) has been recently employed for urea detection in alkaline media, reaching a sub- μM limit of detection, and has also been assessed for urea determination from human urine [58]. If the generation of potentially harmful side-products of UOR is, *a priori*, not a problem for urea sensing applications, more research is still needed in this field to enable real-life use of UOR-based electrochemical or photoelectrochemical sensors. In particular, the evaluation of sensor performance in biologically or industrially relevant samples should be further investigated.

Best practices and conclusion

Despite the relatively long-lasting interest and the knowledge on urea oxidation in the field of artificial kidneys (Section [Clinical applications of UOR: artificial kidneys](#)), all UOR reaction products in conventional conditions (Table 1) were not fully identified until very recently [4,5]. These findings revealed that the initially assumed “sustainable pathway” (Reaction (3)) leading to harmless N₂ and dissolved CO₂ (in the form of carbonate ions) represented only a small fraction of the oxidation pathway with widely employed standard UOR catalysts. Accordingly, when developing real-life applications of UOR for power-to-X, considerable research is needed to inhibit the formation of soluble harmful substances (NO₂[−] and NCO[−]).

Indeed, since the late 2000s, UOR has shown increasing promise for power-to-H₂ conversion coupled with wastewater treatment, has been extensively studied for PEC solar-to-H₂ conversion, and is being considered for other power-to-X schemes involving CO₂ or N₂ reduction. Progress has been achieved in this field including a considerable improvement in operation stability (up to 50 h) [28,29] or efficient interfacing of UOR catalysts with semiconductor photoelectrodes (Section [Sun-to-H₂](#)) [11,13,30]. Besides power-to-H₂, we have also discussed the strong potential of UOR for clinical and sensing applications. Considering that a widely admitted and potentially considerable added value of UOR is the use of urea-rich waste aqueous feedstocks and their purification (Fig. 1a), from now on, it is crucial to analyze gas phase and liquid phase reaction products in new research works devoted to UOR. This is especially important when this remediation effect is claimed to take place because strong evidence from many groups [4,5,22,25,30,31,47] now suggests that it is unlikely to happen in application-based conditions with conventional Ni-based catalysts.

In conclusion, despite the discovery of overoxidation side products, a remarkable bounce has already allowed considerable improvement of the Faradaic efficiency for N₂ formation through the “sustainable pathway” *via* surface modification of conventional UOR catalysts [4,5]. Thus, the next shift of UOR research should be

given to catalyst selectivity, particularly in light of recent results obtained on bimetallic catalysts [5]. Also, as electrolyte composition has been reported to affect UOR performance [59], its effect on selectivity deserves to be investigated. Another aspect that should be studied is how the pH drop associated with UOR (Reaction (3,6,7)) affects long-term electrolysis. Although it seems that the presence of urea in the electrolyte does not affect considerably Faradaic efficiency for H₂ generation (Reaction (1)) [28], the byproducts originating from the reduction of NO_x[−] produced by overoxidation (Reactions (6,7)) should be clarified. In this frame, one can think that electrochemical reduction may also be a solution to valorize the undesired NO_x[−] products. Overall, the “UOR rebirth” is extremely promising for future research, as it suggests that considerable improvements may be reached soon in the field of UOR.

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.

Data availability

Data will be made available on request.

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- * of special interest
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