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## Review Article

## Cathodic corrosion: 21st century insights into a 19th century phenomenon

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## Abstract

Cathodic corrosion is an enigmatic electrochemical process that etches metallic electrodes at potentials below 0 V *versus* the normal hydrogen electrode. Although this phenomenon was discovered in the late 1800s by Fritz Haber, it remained mostly unnoticed during the 20th century and only attracted increased attention in the past decade. This recent attention has generated marked improvements in both the fundamental knowledge and the applications of cathodic corrosion. Fundamental new insights were gained into the effects and possible reaction intermediates of cathodic corrosion. Complementing these insights, recent advances involve applications of cathodic corrosion for nanoparticle synthesis and electrocatalyst modification. Both these applied and fundamental advances will be discussed in this short review on cathodic corrosion.

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## Keywords

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## Introduction

The term ‘corrosion’ refers to a wide range of destructive electrochemical phenomena that are broadly defined as the degradation of materials that interact with their environment [1]. Reflecting this broad definition of corrosion, its effects can range from common and innocent cosmetic blemishes on shiny bicycles and cars, to rare but catastrophic failures of bridges and oil pipelines. Owing to

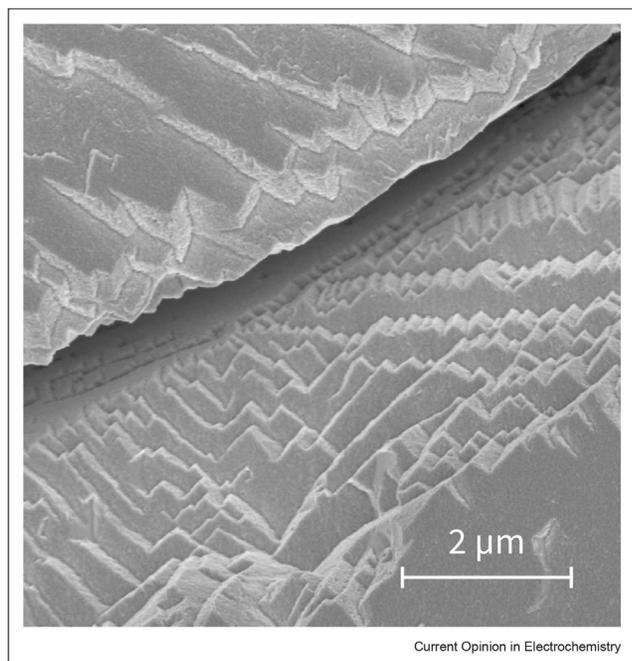
its widespread nature, corrosion is estimated to cost more than 3% of the global gross domestic product [2].

In science, the destructive role of corrosion was acknowledged as early as 1824, when Sir Humphry Davy worked ‘*on the corrosion of copper sheeting by sea water, and on methods of preventing this effect; and on their application to ships of war and other ships*’ [3]. This work is recognized as the discovery of cathodic protection, which is still an often-used corrosion prevention method [4]. Briefly, cathodic protection involves lowering the electrochemical potential of a metal, such that oxidation of the metal becomes thermodynamically unfavorable. The absence of oxidation might suggest that cathodic protection stabilizes a metal in its elemental state indefinitely. Although tempting, this suggestion is not always correct: at sufficiently negative potentials, metals can start corroding through a phenomenon known as *cathodic corrosion* [5].

Intriguingly, cathodic corrosion was first reported as early as the late 19th century, when Fritz Haber observed particulate clouds dispersing from cathodically polarized metals [6,7]. Haber ascribed these clouds to the formation and subsequent destruction of alloys between the corroded metal and electrolyte cations such as Na<sup>+</sup> and K<sup>+</sup>. Cathodic corrosion or ‘disintegration’ was briefly revisited in the mid-1900s [8–10] but otherwise remained mostly overlooked during the 20th century.

Fortunately, the 21st century brought renewed attention to cathodic corrosion: in 2011, the first recent work to recognize cathodic corrosion as such was published [5]. This work examined a protocol that generates metallic nanoparticles by applying an alternating current to a metallic wire. Although nanoparticle formation used to be ascribed to *anodic* corrosion during the positive alternating current half-cycle [11,12], Yanson et al. [5] unambiguously demonstrated significant nanoparticle formation during the negative half-cycle, i.e. during *cathodic* corrosion. Furthermore, the work revealed the formation of remarkable geometric etch features, as illustrated in [Figure 1](#). These results spurred follow-up research that was summarized in two reviews in 2013 [13,14]. However, both the active species and the reaction mechanism of cathodic corrosion remained largely unknown at the time.

Figure 1



Scanning electron micrograph of a cathodically corroded polycrystalline platinum electrode. The image features a boundary between two crystal grains, on which etching produced large geometrical patterns. Etching was performed in 5 M NaOH, by applying a 0.5 Hz square wave with potential limits of  $-1.0$  V and  $+2.0$  V *versus* the reversible hydrogen electrode for 2 min.

Since the 2013 reviews of cathodic corrosion, significant research efforts have aimed to both understand and use this 120-year-old phenomenon. In both regards, substantial progress has been made. The present article will briefly summarize this progress, thus highlighting important improvements in the understanding of cathodic corrosion, as well as novel applications of this counterintuitive electrochemical phenomenon.

### Scope

The name ‘cathodic corrosion’ suggests two features about its underlying process: it is reductive (cathodic) in nature and morphologically alters (corrodes) the material being affected by it. Many reactions fit this description, such as the conversion of carbon nanotubes to ‘nanotubide’ [15]; copper carboxylation in aprotic solvents [16]; Sn-SnO<sub>x</sub> nanoparticle formation in ionic liquids [17]; ion insertion into platinum in aprotic solvents [18,19]; and reactions between (earth) alkali(ne) metals and gold/platinum [20]. Although these processes are interesting cathodic reactions that alter materials and, in the latter two examples, allow for metallic anions such as aurides and platinides to form [21–23], it is beyond the scope of this Review to discuss all such reactions in detail. Instead, the present article will focus

exclusively on the cathodic corrosion of metals in aqueous environments.

This focus will be three-pronged. First, the following section will discuss the fundamentals of cathodic corrosion, followed by a discussion of applications of cathodic corrosion. These Fundamentals and Applications sections will then inform the final Outlook section of the Review.

### Fundamentals

From a fundamental perspective, cathodic corrosion is assumed to proceed through the mechanism illustrated for platinum in Figure 2 [13]. In Figure 2, panel 1 visualizes the starting state of cathodic corrosion: a Pt surface in an NaOH solution, polarized below 0 V *vs.* the reversible hydrogen electrode (RHE). Under these conditions, Pt vigorously evolves hydrogen gas and is covered with adsorbed hydrogen atoms [24]. A partial monolayer of Na<sup>+</sup> is likely adsorbed as well [25]. In these circumstances, an unknown and presumably anionic species dissolves into the working solution (panel 2). Although the identity of this species is unknown, it is likely cation-stabilized because a nonprotic electrolyte cation is required to enable cathodic corrosion [5]. After its formation, the cation-stabilized anion moves away from the Pt surface until it encounters a water molecule (panel 3). In this encounter, the water is reduced to H<sub>2</sub> and OH<sup>-</sup>, whereas the anion is oxidized back to neutral platinum. These Pt atoms can then redeposit onto their native surface or nucleate in solution into nanoparticles (panel 4).

As illustrated previously, the reaction mechanism hinges on the formation of an unknown species. This species has been challenging to observe through *operando* or *in situ* spectroscopy: these techniques are often incompatible with the negative potentials at which cathodic corrosion occurs or with the vigorous hydrogen evolution at these potentials [26]. Other techniques require samples such as gold–platinum core–shell particles that are likely consumed rapidly during cathodic corrosion [27]. Furthermore, the main corrosion intermediate is extremely short-lived and therefore impossible to isolate and study directly [13]. Instead, most research has investigated cathodic corrosion *indirectly*, by examining its effects on electrodes or by studying the nanoparticles that it creates (Figure 2, panel 4).

Such studies revealed a critical property of cathodic corrosion: it occurs anisotropically, thus favoring the creation of specific surface sites. This anisotropy was first utilized by creating (100)-oriented Pt nanoparticles [28]. Notably, the same (100) etching preference is imprinted on the platinum surface from which nanoparticles are formed [29]. For surfaces, the etching preference generates (100)-oriented

Figure 2

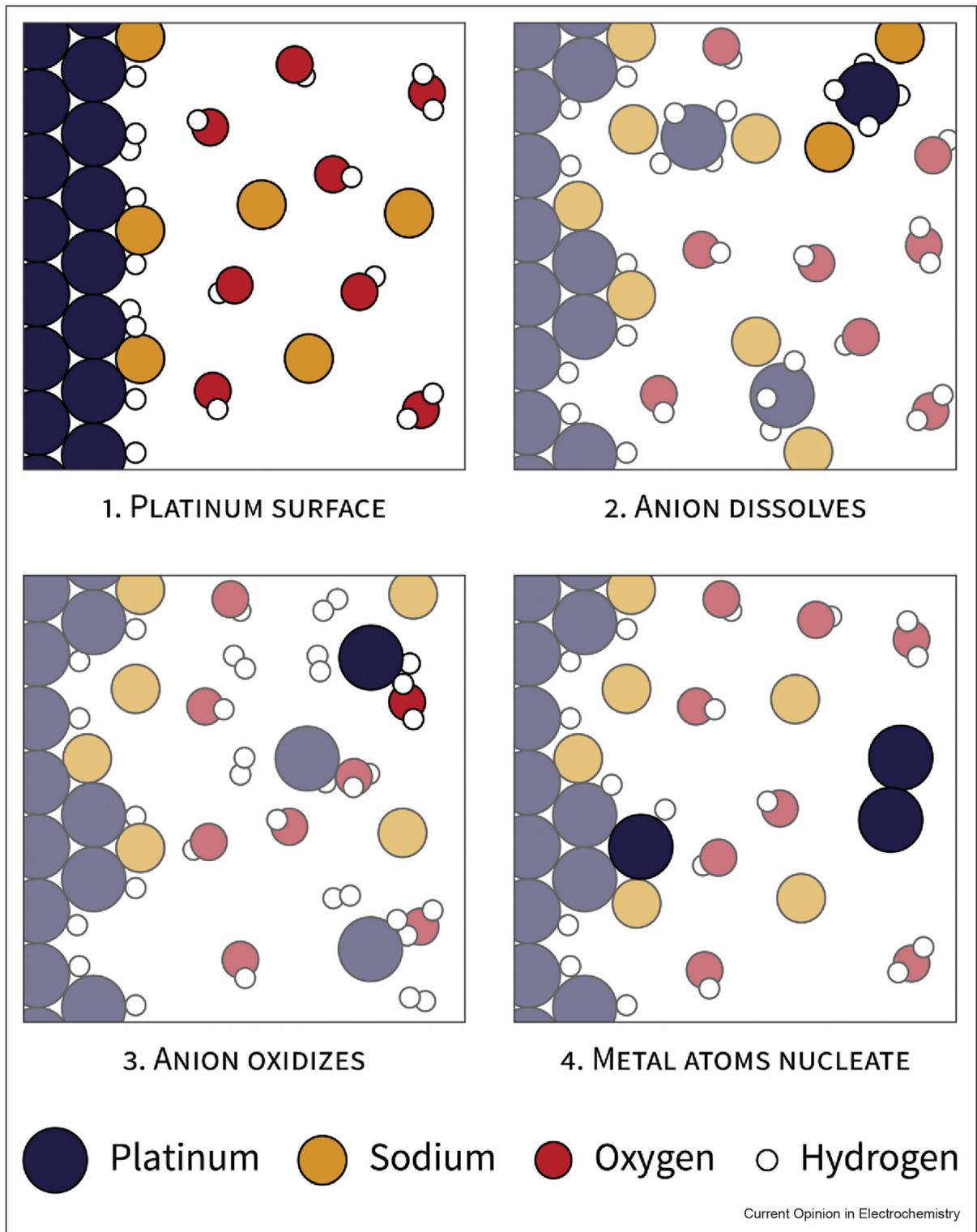
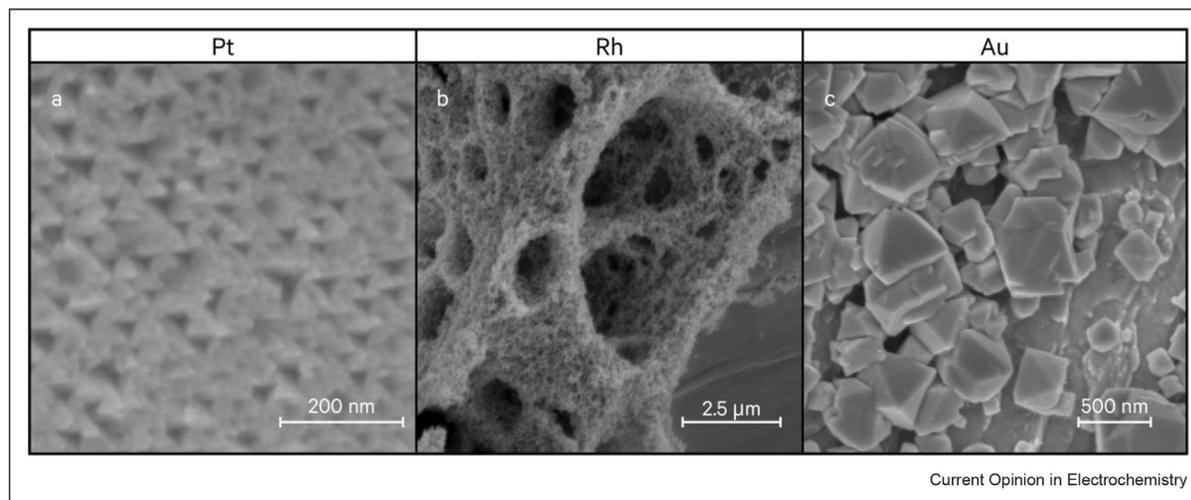


Illustration of the hypothesized cathodic corrosion mechanism, using Pt as an example. This corrosion occurs at potentials where the platinum is covered by adsorbed hydrogen and cations like  $\text{Na}^+$  (panel 1). At these potentials, hydrogen evolution occurs as well. Under these conditions, some Pt converts into an unknown cation-stabilized anion (panel 2), which dissolves (In contrast to what is drawn in the figure, the anion might consist of more than one platinum atom). Eventually, the anion encounters water and is oxidized back to atomic platinum (panel 3). This platinum can then redeposit on the electrode or nucleate into nanoparticles (panel 4).

Figure 3



Scanning electron micrographs of Pt, Rh, and Au, corroded for 1 min in 5 M NaOH. Pt and Rh were corroded at  $-0.8$  V vs. RHE, whereas Au was corroded at  $-1.5$  V vs. RHE. Images collected as described previously [25].

equilateral triangles when corroding into (111) facets at moderate potentials (Figure 3a) [30]. Interestingly, the (100) etching preference generates differently shaped etch pits on other crystal planes, which can grow into fractal-like shapes at more negative corrosion potentials and prolonged corrosion times [31]. Similar crystal plane variations were found for Au, though no fractal growth patterns have been observed for this metal [32].

The dissimilarities between Pt and Au highlight a metal-dependent response to cathodic corrosion. Such differences are especially apparent when corroding various metals under similar conditions (Figure 3). For example, although Pt and Rh preferentially form (100) facets through corrosion in 10 M NaOH, Au primarily exposes (111) facets [30,33]. Under the same conditions, the corrosion onset also varies by metal: Pt and Rh commence corrosion at  $-0.4$  V vs. RHE, whereas Au starts at  $-0.7$  V vs. RHE. Similar variations appear when producing nanoparticles through cathodic corrosion: each metal produces differently sized nanoparticles, and some metals corrode in certain working electrolytes where other metals do not [14,34]. We assume that these differences are related to the chemical and geometrical structure of the cathodic corrosion intermediates (Figure 2).

The electrolyte dependence hints at the importance of the corrosion electrolyte and, specifically, the electrolyte cation [14]. These cations enable cathodic corrosion [5] and affect the formation rate and orientation of cathodically produced nanoparticles [28,29]. Electrolyte cations also affect corroded surfaces. This was demonstrated for Pt, Rh, and Au in LiOH, NaOH, and KOH

solutions [25], for which the cation concentration and identity each affect the corrosion facet preference. Furthermore, corrosion starts at less negative potentials when increasing the cation concentration, and when changing the cation from  $\text{Li}^+$  to  $\text{Na}^+$  and  $\text{K}^+$ . These cation effects were qualitatively explained by theoretical computations, which suggest that cations adsorb to corroding surfaces [25]. However, these calculations do not capture the exact corrosion differences between cations. It is therefore likely that additional factors affect cathodic corrosion.

One of these factors might be atomic hydrogen, which adsorbs to Pt surfaces below  $\sim 0.3$  V vs. RHE [35,36]: adsorbed hydrogen ( $\ast\text{H}$ ) might drive surface area creation during cathodic corrosion [25]. Even before the onset of cathodic corrosion, sufficient amounts of adsorbed hydrogen can induce platinum step edge reconstruction, converting straight (111)-oriented straight step edges into roughened step edges with a (local) (100) orientation [37]. This step edge roughening could be considered a prelude to terrace roughening at more negative corrosion potentials. The essential role of  $\ast\text{H}$  would also be consistent with recent results from Elnagar et al. [38] for cathodic Au corrosion in mixtures of water and nonaqueous solvents: this study found no cathodic corrosion in absence of water. Because water would be the main hydrogen source during cathodic corrosion, these results in absence of water support the hypothesized relevance of  $\ast\text{H}$ .

Adsorbed hydrogen therefore joins the electrolyte cations and the corroded metal as one of the three chemical species that likely play a key role during cathodic

corrosion. During corrosion, these species might combine into a ternary metal hydride, such as  $\text{Na}_2\text{PtH}_4$ ,  $\text{Na}_3\text{RhH}_6$ , or  $\text{NaAuH}_2$  [39–41]. Such hydride formation resembles cation incorporation in noble metals [10], which has previously been suggested to drive cathodic corrosion [42]. In addition, the formation of ternary metal hydrides would parallel the conversion of Pb and Sn to  $\text{PbH}_2$  or  $\text{SnH}_4$  [8,9,43–45]. Although presently unconfirmed, the possibility of ternary metal hydrides during cathodic corrosion therefore seems plausible. This hypothesis could be tested spectroscopically, if challenges related to hydrogen evolution during cathodic corrosion are overcome.

Although the exact cathodic corrosion mechanism has so far remained elusive, cathodic corrosion can morphologically alter metallic surfaces at potentials as mild as  $-0.4$  V *vs.* RHE in highly alkaline media [30]. Such potentials are frequently encountered during  $\text{CO}_2$  reduction or the reduction of organic molecules [46,47], which suggests that catalyst surfaces can change cathodically during electrocatalysis. In fact, cathodic corrosion has been observed during CO reduction on Au [32], Cu surfaces reconstruct anisotropically during  $\text{CO}_2$  reduction [48,49], and Sn electrocatalysts display anisotropic pits after nitrate reduction [44]. Such structural changes could affect electrocatalysts because a catalyst's structure often affects its performance [50,51]. In this respect, cathodic corrosion can be much more detrimental to electrode stability than anodic corrosion, especially for metals such as platinum [30].

## Applications

Conversely, the structure-altering effects of cathodic corrosion can also benefit electrocatalysis. These benefits are usually exploited by using cathodic corrosion to synthesize a broad range of nanomaterials [34].

Examples include the production of oxide materials, which are presumed to form cathodically and oxidize rapidly afterward. These materials, such as  $\text{H}_2\text{WO}_4$ ,  $\text{TiO}_2$ , and  $\text{BiVO}_4$ , can be used as photocatalysts [52]. More complex photocatalysts can be created as well, by corroding alloy electrodes instead of monometallic ones. This approach recently yielded a series of metal-doped titanate photocatalysts [53].

Alloy corrosion can also produce metallic alloy nanoparticles, as was initially demonstrated by producing PtRh alloys with tunable composition [54]. Although great care should be taken in verifying the local composition of such nanoparticles [55], there are many nanoalloys that can be created cathodically [34,56]. Nanoalloys can even be created if an alloyed sacrificial electrode is unavailable because the alloy elements are immiscible on the bulk scale [57]. In this case, one can corrode a monometallic electrode in the presence of a

reducible cation in solution. This cation is coreduced during cathodic corrosion to create classically immiscible alloys such as PtBi and PtPb [58].

Besides synthesizing 'complex' alloy and oxide systems, the production of 'simpler' monometallic nanoparticles also benefits from cathodic corrosion. For these particles, the final particle orientation and size can be tuned by varying the corrosion current [59] and corrosion electrolyte [28,29]. By tweaking these variables, one can convert a metal such as Pt to (100)-rich particles for ammonia oxidation [28] or defect-rich Pt nanoparticles for enhanced oxygen reduction [60].

Interestingly, a similar approach can modify existing bulk or nanoparticulate electrodes. For example, cathodic corrosion can tailor both the catalytic activity of Pt(111) toward oxygen reduction and its selectivity toward glycerol oxidation [61]. Similarly, cathodic corrosion can disperse and regenerate nanoparticle catalysts [62]. The benefits of cathodic corrosion therefore extend beyond nanoparticle synthesis alone.

## Outlook

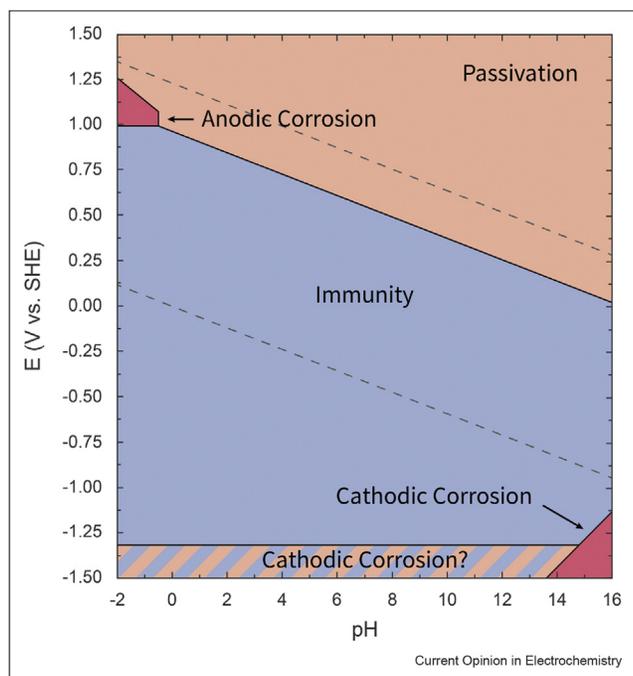
Cathodic corrosion can produce milligrams of nanoparticles in minutes or hours, using a simple voltage source and without requiring capping agents that might affect catalytic performance [63]. Illustrating this point, elegant adaptations of cathodic corrosion have already produced a range of metallic, alloyed and metal oxide nanocatalysts [45,52–54,56,58,60,64]. At the same time, we recognize a current scarcity of systematic research on the parameters that impact the size, shape, and composition of cathodically generated nanoparticles. Understanding these parameters is crucial for the widespread deployment of cathodic corrosion, which depends on a detailed understanding of its advantages over other nanoparticle synthesis methods.

This development will therefore benefit greatly from further fundamental cathodic corrosion studies. Such studies have already provided guidelines for nanoparticle production and electrode modification [14,25], and further work should expand these guidelines. Furthermore, this fundamental work might eventually reveal the identity of the cathodic corrosion intermediate.

Pinpointing this intermediate is also paramount for understanding metallic surfaces at industrially relevant cathodic potentials. Ideally, such understanding would be summarized in updated Pourbaix diagrams. Although these diagrams typically feature the metallic state as the most reduced one for transition metals [43], they might eventually incorporate cathodic corrosion products.

To inspire such updated diagrams, we have provided a tentative version in Figure 4. This figure is based on the

Figure 4



Simplified Pourbaix diagram for platinum, adapted from literature [43]. The upper and lower dashed line represent the conversion from water to oxygen and hydrogen, respectively. The corrosion onset potentials were explicitly determined in 1, 5, and 10 M NaOH [25,30] with 0.1 V accuracy. These potentials were used to construct an approximate boundary between 'Immunity' and 'Cathodic Corrosion' in the present diagram, which should strictly be used for illustrative purposes.

standard Pourbaix diagram for Pt [43] but incorporates the known cathodic Pt corrosion onset in alkaline solutions [25,30]. At lower pH values, cathodic corrosion also occurs [5,34], which Figure 4 visualizes with a shaded area, in lieu of established onset potentials. Finding these onsets is highly desirable but equally challenging due to the hydrogen evolution that accompanies cathodic corrosion: hydrogen evolution produces  $\text{OH}^-$ , which significantly increases the near-electrode pH with respect to the bulk pH [65,66]. Reflecting this fact, the cathodic corrosion onset at lower pH values is illustrated for a hypothetically high near-electrode pH, resulting in a constant onset with respect to the normal hydrogen electrode.

In addition, it should be noted that Pourbaix diagrams describe systems in thermodynamic equilibrium. In this sense, it is not strictly correct to include cathodic corrosion onset potentials similar to those in Figure 4: these onset potentials were determined for systems with unknown concentrations of metastable reaction species and at conditions where the near-electrode pH differs from the bulk pH. Besides identifying onset potentials, future studies should therefore also attempt to establish cathodic corrosion equilibrium potentials.

Furthermore, updated Pourbaix diagrams might explicitly incorporate the role of electrolyte cations. This could be achieved by assuming a constant background concentration of  $\text{Na}^+$  [67], or by incorporating a cation concentration axis. Despite the notable points of improvement in the current illustrative Pourbaix diagram, future updated Pourbaix diagrams will help express that the cathodic behavior of metals can be more complex than suggested by the widespread use of cathodic protection.

## Conclusions

Summarizing, cathodic corrosion is an electrochemical process that etches metallic electrodes and produces nanoparticles at (not so very) negative potentials. As of this writing, cathodic corrosion has been established to occur as early  $-0.4$  V *vs.* RHE in 10 M NaOH, in tandem with electrochemical hydrogen evolution. Cathodic corrosion in aqueous media is currently hypothesized to be mediated by ternary metal hydrides, which may generate pre-nucleation clusters in solution that facilitate nanoparticle formation under suitable conditions. Although detailed confirmation of this hypothesis is still pending, the past years have seen cathodic corrosion being used for producing nanoparticles and bulk electrodes with enhanced electrocatalytic properties. If these improvements toward fundamentally understanding cathodic corrosion and its nanoparticle production continue, they will firmly cement this 19th century phenomenon into modern 21st century electrochemistry.

## Author contributions

TJPH contributed to Conceptualization, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. MTMK contributed to Conceptualization, Writing – Original Draft, Writing – Review & Editing, and 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.

## References

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Bard AJ, Inzelt G, Scholz F: *Electrochemical dictionary*. 2nd ed. Heidelberg: Springer Berlin; 2012.
2. Hou B, Li X, Ma X, Du C, Zhang D, Zheng M, Xu W, Lu D, Ma F: **The cost of corrosion in China**, *npj Mater. Degrad* 2017, 1:4.
3. Davy H: **On the corrosion of copper sheeting by sea water, and on methods of preventing this effect; and on their**

- application to ships of war and other ships. *Phil Trans Roy Soc Lond* 1824, **114**:151–158.
4. Baeckmann Wv, Schwenk W, Prinz W: *Handbook of cathodic corrosion protection*. 3rd ed. Elsevier; 1997.
  5. Yanson AI, Rodriguez P, Garcia-Araez N, Mom RV, Tichelaar FD, ●● Koper MTM: **Cathodic corrosion: a quick, clean, and versatile method for the synthesis of metallic nanoparticles**. *Angew Chem Int Ed* 2011, **50**:6346–6350.  
This article is, to our knowledge, the first 21st century work to describe cathodic corrosion as such.
  6. Haber F: **Über Elektrolyse der Salzsäure nebst Mitteilungen über kathodische Formation von Blei. III. Mitteilung**. *Z Anorg Chem* 1898, **16**:438–449.
  7. Haber F: **The phenomenon of the formation of metallic dust from cathodes**. *Trans Am Electrochem Soc* 1902, **2**:189–196.  
This article is one of the first English-language works describing cathodic corrosion.
  8. Salzberg HW: **Cathodic lead disintegration and hydride formation**. *J Electrochem Soc* 1953, **100**:146.
  9. Salzberg HW, Mies F: **Cathodic disintegration of tin**. *J Electrochem Soc* 1958, **105**:64.
  10. Kabanov BN, Astakhov II, Kiseleva IG: **Formation of crystalline intermetallic compounds and solid solutions in electrochemical incorporation of metals into cathodes**. *Electrochim Acta* 1979, **24**:167–171.
  11. Liu J, Huang W, Chen S, Hu S: **Facile electrochemical dispersion of bulk Rh into hydrosols**. *Int J Electrochem Sci* 2009, **4**:1302–1308.
  12. Huang W, Chen S, Zheng J, Li Z: **Facile preparation of Pt hydrosols by dispersing bulk Pt with potential perturbations**. *Electrochem Commun* 2009, **11**:469–472.
  13. Yanson YI, Yanson AI: **Cathodic corrosion. I. Mechanism of corrosion via formation of metal anions in aqueous medium**. *Low Temp Phys* 2013, **39**:304–311.  
The first instalment of a detailed two-part review of cathodic corrosion.
  14. Yanson AI, Yanson YI: **Cathodic corrosion. II. Properties of nanoparticles synthesized by cathodic corrosion**. *Low Temp Phys* 2013, **39**:312–317.  
The second instalment of a detailed two-part review of cathodic corrosion.
  15. Hodge SA, Fogden S, Howard CA, Skipper NT, Shaffer MSP: **Electrochemical processing of discrete single-walled carbon nanotube anions**. *ACS Nano* 2013, **7**:1769–1778.
  16. Simonet J: **Large-scale cathodic carboxylation of copper surfaces**. *Electrochem Commun* 2017, **76**:67–70.
  17. Lu F, Ji X, Yang Y, Deng W, Banks CE: **Room temperature ionic liquid assisted well-dispersed core-shell tin nanoparticles through cathodic corrosion**. *RSC Adv* 2013, **3**:18791–18793.
  18. Simonet J, Labaume E, Rault-Berthelot J: **On the cathodic corrosion of platinum in the presence of iodides in dry aprotic solvents**. *Electrochem Commun* 1999, **1**:252–256.
  19. Ghilane J, Guilloux-Viry M, Lagrost C, Hapiot P, Simonet J: **Cathodic modifications of platinum surfaces in organic solvent: reversibility and cation type effects**. *J Phys Chem B* 2005, **109**:14925–14931.
  20. Jansen M: **Effects of relativistic motion of electrons on the chemistry of gold and platinum**. *Solid State Sci* 2005, **7**:1464–1474.
  21. Ghilane J, Lagrost C, Guilloux-Viry M, Simonet J, Delamar M, Mangeney C, Hapiot P: **Spectroscopic evidence of platinum negative oxidation states at electrochemically reduced surfaces**. *J Phys Chem C* 2007, **111**:5701–5707.
  22. Karpov A, Konuma M, Jansen M: **An experimental proof for negative oxidation states of platinum: ESCA-measurements on barium platinides**. *Chem Commun* 2006:838–840.
  23. Jansen M: **The chemistry of gold as an anion**. *Chem Soc Rev* 2008, **37**:1826.
  24. Jerkiewicz G: **Electrochemical hydrogen adsorption and absorption. Part 1: under-potential deposition of hydrogen**. *Electrocatalysis* 2010, **1**:179–199.
  25. Hersbach TJP, McCrum IT, Anastasiadou D, Wever R, Calle-Vallejo F, Koper MTM: **Alkali metal cation effects in structuring Pt, Rh, and Au surfaces through cathodic corrosion**. *ACS Appl Mater Interfaces* 2018, **10**:39363–39379.  
This article provides extensive characterization of the cathodic corrosion of Pt, Rh and Au under various working conditions.
  26. Osawa M, Tsushima M, Mogami H, Samjeské G, Yamakata A: **Structure of water at the electrified platinum–water interface: a study by surface-enhanced infrared absorption spectroscopy**. *J Phys Chem C* 2008, **112**:4248–4256.
  27. Jiang Y-X, Li J-F, Wu D-Y, Yang Z-L, Ren B, Hu J-W, Chow YL, Tian Z-Q: **Characterization of surface water on Au core Pt-group metal shell nanoparticles coated electrodes by surface-enhanced Raman spectroscopy**. *Chem Commun* 2007:4608.
  28. Duca M, Rodriguez P, Yanson AI, Koper MTM: **Selective electrocatalysis on platinum nanoparticles with preferential (100) orientation prepared by cathodic corrosion**. *Top Catal* 2014, **57**:255–264.
  29. Yanson AI, Antonov PV, Rodriguez P, Koper MTM: **Influence of the electrolyte concentration on the size and shape of platinum nanoparticles synthesized by cathodic corrosion**. *Electrochim Acta* 2013, **112**:913–918.
  30. Hersbach TJP, Yanson AI, Koper MTM: **Anisotropic etching of platinum electrodes at the onset of cathodic corrosion**. *Nat Commun* 2016, **7**:12653.
  31. Arulmozhi N, Hersbach TJP, Koper MTM: **Nanoscale morphological evolution of monocrystalline Pt surfaces during cathodic corrosion**. *Proc Natl Acad Sci Unit States Am* 2020, <https://doi.org/10.1073/pnas.2017086117>.
  32. Raaijman SJ, Arulmozhi N, Koper MTM: **Anisotropic Cathodic Corrosion of Gold Electrodes in the Absence and Presence of Carbon Monoxide**. *J Phys Chem C* (2020), accepted for publication
  33. Hersbach TJP, Mints VA, Calle-Vallejo F, Yanson AI, Koper MTM: **Anisotropic etching of rhodium and gold as the onset of nanoparticle formation by cathodic corrosion**. *Faraday Discuss* 2016, **193**:207–222.
  34. Feng J, Chen D, Sediq AS, Romeijn S, Tichelaar FD, Jiskoot W, Yang J, Koper MTM: **Cathodic corrosion of a bulk wire to nonaggregated functional nanocrystals and nanoalloys**. *ACS Appl Mater Interfaces* 2018, **10**:9532–9540.
  35. Kunimatsu K, Senzaki T, Samjeské G, Tsushima M, Osawa M: **Hydrogen adsorption and hydrogen evolution reaction on a polycrystalline Pt electrode studied by surface-enhanced infrared absorption spectroscopy**. *Electrochim Acta* 2007, **52**:5715–5724.
  36. Stoerzinger KA, Favaro M, Ross PN, Yano J, Liu Z, Hussain Z, Crumlin EJ: **Probing the surface of platinum during the hydrogen evolution reaction in alkaline electrolyte**. *J Phys Chem B* 2018, **122**:864–870.
  37. McCrum IT, Bondue CJ, Koper MTM: **Hydrogen-induced step-edge roughening of platinum electrode surfaces**. *J Phys Chem Lett* 2019, **10**:6842–6849.
  38. Elnagar MM, Hermann JM, Jacob T, Kibler LA: **Faceting and nanostructuring of gold surfaces through cathodic corrosion: role of cationic electrolyte species and water**. In *ECSS meet. Abstr.*; 2020. 1011–1011.
  39. Firman TK, Landis CR: **Structure and electron counting in ternary transition metal hydrides**. *J Am Chem Soc* 1998, **120**:12650–12656.
  40. Wang X, Andrews L: **Gold is noble but gold hydride anions are stable**. *Angew Chem Int Ed* 2003, **42**:5201–5206.
  41. Rahm M, Hoffmann R, Ashcroft NW: **Ternary gold hydrides: routes to stable and potentially superconducting compounds**. *J Am Chem Soc* 2017, **139**:8740–8751.

42. Leontyev I, Kuriganova A, Kudryavtsev Y, Dkhil B, Smirnova N:  
 • **New life of a forgotten method: electrochemical route toward highly efficient Pt/C catalysts for low-temperature fuel cells.** *Appl Catal A Gen* 2012, **431–432**:120–125.

This work utilizes cathodic corrosion to produce carbon-supported nanoparticles, and suggests the incorporation of sodium atoms into the sacrificial electrode during cathodic corrosion.

43. Pourbaix M: *Atlas of electrochemical equilibria in aqueous solutions*. 2nd ed. National Association of Corrosion Engineers; 1974.
44. Katsounaros I, Ipsakis D, Polatides C, Kyriacou G: **Efficient electrochemical reduction of nitrate to nitrogen on tin cathode at very high cathodic potentials.** *Electrochim Acta* 2006, **52**:1329–1338.
45. Pavesi D, van de Poll RCJJ, Krasovic JL, Figueiredo M, Gruter G-JM, Koper MTMM, Schouten KJP: **Cathodic disintegration as an easily scalable method for the production of Sn- and Pb-based catalysts for CO<sub>2</sub> reduction.** *ACS Sustain Chem Eng* 2020, **8**:15603–15610.
46. Xie C, Niu Z, Kim D, Li M, Yang P: **Surface and interface control in nanoparticle catalysis.** *Chem Rev* 2020, **120**:1184–1249.
47. Carneiro J, Nikolla E: **Electrochemical conversion of biomass-based oxygenated compounds.** *Annu Rev Chem Biomol Eng* 2019, **10**:85–104.
48. Kim Y-G, Baricuatro JH, Javier A, Gregoire JM, Soriaga MP: **The evolution of the polycrystalline copper surface, first to Cu(111) and then to Cu(100), at a fixed CO<sub>2</sub>RR potential: a study by operando EC-STM.** *Langmuir* 2014, **30**:15053–15056.
49. Kim Y-G, Javier A, Baricuatro JH, Torelli D, Cummins KD, Tsang CF, Hemminger JC, Soriaga MP: **Surface reconstruction of pure-Cu single-crystal electrodes under CO-reduction potentials in alkaline solutions: a study by seriatim ECSTM-DEMS.** *J Electroanal Chem* 2016, **780**:290–295.
50. Koper MTM: **Structure sensitivity and nanoscale effects in electrocatalysis.** *Nanoscale* 2011, **3**:2054–2073.
51. Strasser P, Gliech M, Kuehl S, Moeller T: **Electrochemical processes on solid shaped nanoparticles with defined facets.** *Chem Soc Rev* 2018, **47**:715–735.
52. Kromer ML, Monzó J, Lawrence MJ, Kolodziej A, Gossage ZT, Simpson BH, Morandi S, Yanson A, Rodríguez-López J, Rodríguez P: **High-throughput preparation of metal oxide nanocrystals by cathodic corrosion and their use as active photocatalysts.** *Langmuir* 2017, **33**:13295–13302.
53. Lawrence MJ, Celorrio V, Shi X, Wang Q, Yanson A, Adkins NJEE, Gu M, Rodríguez-López J, Rodríguez P: **Electrochemical synthesis of nanostructured metal-doped titanates and investigation of their activity as oxygen evolution photoanodes.** *ACS Appl Energy Mater* 2018, **1**:acsam.8b00873.

This work utilizes cathodic corrosion to produce a series of metal-doped titanate nanoparticles.

54. Rodríguez P, Tichelaar FD, Koper MTM, Yanson AI: **Cathodic corrosion as a facile and effective method to prepare clean metal alloy nanoparticles.** *J Am Chem Soc* 2011, **133**:17626–17629.

55. Hersbach TJP, Kortlever R, Lehtimäki M, Krttil P, Koper MTM: **Local structure and composition of PtRh nanoparticles produced through cathodic corrosion.** *Phys Chem Chem Phys* 2017, **19**:10301–10308.

56. Fichtner J, Garlyyev B, Watzele S, El-Sayed HA, Schwämmlein JN, Li W-J, Maillard FM, Dubau L, Michalička J, Macak JM, Holleitner A, Bandarenka AS: **Top-down synthesis of nanostructured platinum–lanthanide alloy oxygen reduction reaction catalysts: Pt<sub>x</sub>Pr<sub>y</sub>C as an example.** *ACS Appl Mater Interfaces* 2019, **11**:5129–5135.
57. Palomares-Baez J-P, Panizon E, Ferrando R: **Nanoscale effects on phase separation.** *Nano Lett* 2017, **17**:5394–5401.
58. Bennett E, Monzó J, Humphrey J, Plana D, Walker M, McConville C, Fermin D, Yanson A, Rodríguez P: **A synthetic route for the effective preparation of metal alloy nanoparticles and their use as active electrocatalysts.** *ACS Catal* 2016, **6**:1533–1539.

This work features the use of cathodic corrosion to produce nanoparticles of classically immiscible alloys.

59. Yanson AI, Antonov PV, Yanson YI, Koper MTM: **Controlling the size of platinum nanoparticles prepared by cathodic corrosion.** *Electrochim Acta* 2013, **110**:796–800.
60. Fichtner J, Watzele S, Garlyyev B, Kluge RM, Haimerl F, El-Sayed HA, Li W-J, Maillard FM, Dubau L, Chattot R, Michalička J, Macak JM, Wang W, Wang D, Gigl T, Hugenschmidt C, Bandarenka AS: **Tailoring the oxygen reduction activity of Pt nanoparticles through surface defects: a simple top-down approach.** *ACS Catal* 2020, **10**:3131–3142.

This work utilizes cathodic corrosion to produce nanoparticles that are high in 'concave' defects that aid in oxygen reduction catalysis.

61. Hersbach TJP, Ye C, Garcia AC, Koper MTM: **Tailoring the electrocatalytic activity and selectivity of Pt(111) through cathodic corrosion.** *ACS Catalysis* 2020, <https://doi.org/10.1021/acscatal.0c04016>.
62. Vanrenterghem B, Bele M, Zepeda FR, Šala M, Hodnik N, Breugelmans T: **Cutting the Gordian Knot of electrodeposition via controlled cathodic corrosion enabling the production of supported metal nanoparticles below 5 nm.** *Appl Catal B Environ* 2018, **226**:396–402.
63. Montiel MA, Vidal-Iglesias FJ, Montiel V, Solla-Gullón J: **Electrocatalysis on shape-controlled metal nanoparticles: progress in surface cleaning methodologies.** *Curr Opin Electrochem* 2017, **1**:34–39.
64. Maye S, Girault HH, Peljo P: **Thermally regenerative copper nanoslurry flow batteries for heat-to-power conversion with low-grade thermal energy.** *Energy Environ Sci* 2020: 2191–2199.
65. Ryu J, Surendranath Y: **Polarization-induced local pH swing promotes Pd-catalyzed CO<sub>2</sub> hydrogenation.** *J Am Chem Soc* 2020, **142**:13384–13390.
66. Monteiro MCO, Jacobse L, Touzalin T, Koper MTM: **Mediator-free SECM for probing the diffusion layer pH with functionalized gold ultramicroelectrodes.** *Anal Chem* 2020, **92**:2237–2243.
67. Brookins DG: *Eh-pH diagrams for geochemistry*. Springer-Verlag; 1988.