



**HAL**  
open science

## Highly Reactive Diazenyl Radical Species Evidenced during Aryldiazonium Electroreduction

Laure Pichereau, Laure Fillaud, Nikolaos Kostopoulos, Emmanuel Maisonhaute, Thomas Cauchy, Magali Allain, Jean-Marc Noël, Christelle Gautier, Tony Breton

► **To cite this version:**

Laure Pichereau, Laure Fillaud, Nikolaos Kostopoulos, Emmanuel Maisonhaute, Thomas Cauchy, et al.. Highly Reactive Diazenyl Radical Species Evidenced during Aryldiazonium Electroreduction. *Journal of Physical Chemistry Letters*, 2022, 13 (51), pp.11866-11871. 10.1021/acs.jpcllett.2c03089 . hal-04303155v2

**HAL Id: hal-04303155**

**<https://hal.science/hal-04303155v2>**

Submitted on 23 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - ShareAlike 4.0 International License

# Highly reactive diazenyl radical species evidenced during aryldiazonium electroreduction

Laure Pichereau,<sup>a</sup> Laure Fillaud,<sup>b</sup> Nikolaos Kostopoulos,<sup>c</sup> Emmanuel Maisonhaute,<sup>b</sup> Thomas Cauchy,<sup>a</sup> Magali Allain,<sup>a</sup> Jean-Marc Noël,<sup>c</sup> Christelle Gautier\*<sup>a</sup> and Tony Breton\*<sup>a</sup>

<sup>a</sup> Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F-49000 Angers, France.

<sup>b</sup> Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, 4 Place Jussieu, 75005 Paris, France.

<sup>c</sup> Université Paris Cité, ITODYS, CNRS, F-75013, Paris, France.

---

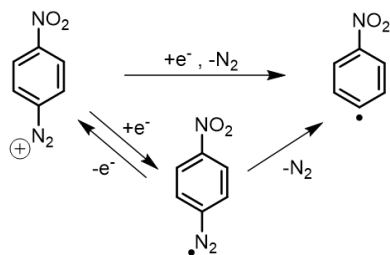
**ABSTRACT:** We report the experimental reassessment of the commonly admitted concerted reduction mechanism for the diazonium electroreduction. Ultrafast cyclic voltammetry was exploited to demonstrate the existence of a stepwise pathway and real-time spectroelectrochemistry experiments allowed to visualize the spectral signature of an evolution product of the nitrophenyldiazenyl radical intermediate. Unambiguous identification of the diazenyl species was achieved by radical trapping followed by X-ray structure resolution. This study brings the evidence of our incomplete understanding of the diazonium electroreduction and calls into question our comprehension of the layer structuration when surface modification is achieved *via* the diazonium electrografting technique. The systematic presence of azo bridges in the nanometric films is likely due to the direct grafting of the aryldiazenyl radical intermediate evidenced here.

---

In 1992, J. Pinson et coll. reported the very first example of carbon modification exploiting the aryldiazonium electroreduction.<sup>1</sup> This new grafting approach, based on the production, and subsequent grafting of reactive aryl radicals, was to become one of the most popular methods to functionalize a broad range of substrates in a very simple way.<sup>2-8</sup> However, the fine description of the layer structuration remains to be developed. Indeed, even if the carbon-substrate bond is now evidenced, nitrogen is systematically detected in the nanometric films in a non-negligible proportion.<sup>9-13</sup> XPS, Raman and TOF-SIMS investigations all converged towards the presence of azo bridges,<sup>14,15</sup> but our scientific community has not yet proposed any alternative mechanistic explanation for their formation.<sup>5,14,16-18</sup> This led us to take a step back and reconsider the sequence that served as a basis for the electrografting technique understanding. Electrochemical reduction of the diazonium compounds has been extensively investigated since the 50's.<sup>19-21</sup> The main objective was to determine whether the electron transfer was coupled to the decomposition into aryl radical and dinitrogen (concerted), or involved an aryldiazenyl radical intermediate (stepwise) (Scheme 1). Several electrochemical investigations on series of para-substituted diazonium have tilted the balance in favour of a stepwise mechanism versus a concerted one by establishing a strong dependence between their reduction potential and the hammet's constant of the substituents.<sup>20,22</sup> Following those first steps, studies were carried out by thermo- and photolysis of azo compounds in the early 70's but did not succeed in discriminating between concerted and non-concerted de-

composition mechanisms.<sup>23-25</sup> The existence of the diazenyl radical transient remained a subject of debate because of conflicting CIDNP (Chemically Induced Dynamic Nuclear Polarization) and ESR (Electron Spin Resonance) interpretations until 1978,<sup>25-28</sup> date on which important evidence of the radical trapping was obtained from the photolysis decomposition of a series of unsymmetric diazene compounds.<sup>29</sup> The development of pulsed radiolysis/photolysis and time-resolved ESR techniques in the 80's definitively confirmed the relative persistence of the aryldiazenyl radical and gave access to decay constants ranging from  $10^5$  to  $10^6$  s<sup>-1</sup>.<sup>30-34</sup> However, first, this intermediate has never been trapped from a diazonium decomposition and second, the highly energetic conditions used to evidence the stepwise decomposition are not transposable to the low driving force exploited for the diazonium electroreduction. Indeed, the driving force typically applied for electrochemical reduction at the peak potential is about 0.07 eV while it is on the order of 3.20 eV when solvated electrons are the reducing species (corresponding to -3.10 V/SCE). In this context, Savéant has worked on the energetic aspect of the bond breaking/formation associated to electron transfers in the early 2000's and stated that the mechanism of a bond cleavage passes from stepwise to concerted as the driving force becomes lower and lower.<sup>35,36</sup> Since this work, the scientific community considered the existence of the sole concerted mechanism in the diazonium electroreduction process.<sup>14,37</sup> Therefore, the grafting technique has been developed and improved with the idea that only aryl radicals can be grafted. In a work published

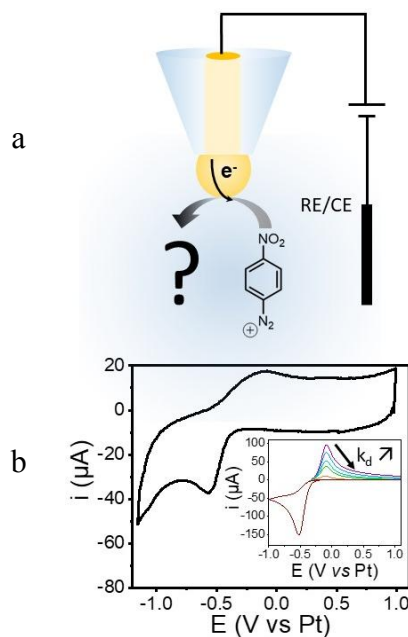
in 2010 focused on the chemical reduction of the nitrobenzene diazonium in homogeneous medium, the trapping of the aryl radical by a ESR active scavenger has strengthened the consensus within the scientific community regarding the reduction of the diazonium salts *via* the concerted mechanism.<sup>38</sup>



**Scheme 1.** Concerted (top) vs stepwise (bottom) mechanism for the diazonium electroreduction.

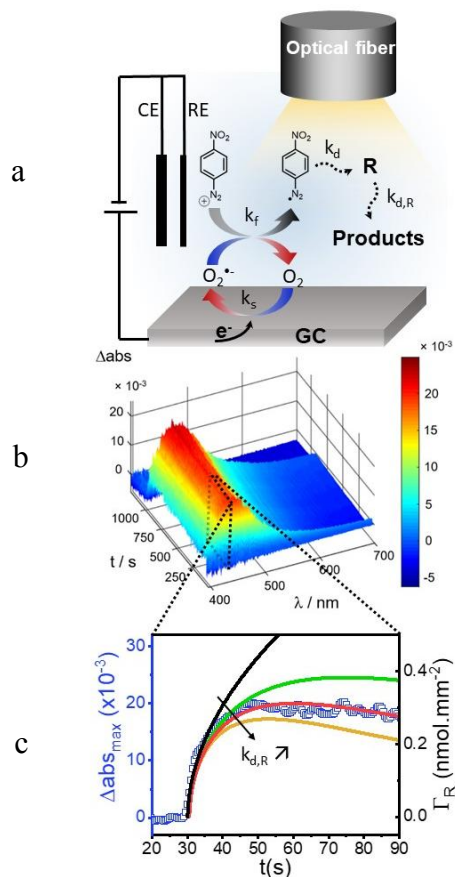
Herein, we experimentally reconsider the mechanistic approach of the diazonium electroreduction to collect evidence that will shed light to whether the reduction follows a stepwise or a concerted route. The 4-nitrobenzene diazonium cation (4-NBD), which widely served as a benchmark for the scientific community to develop the surface functionalization *via* the diazonium reduction, was used in the present work.<sup>18,39,40</sup> The first step consisted to evidence *in-situ* the mechanistic pathway involved in the reduction of the 4-NBD under usual electrografting conditions. Examination of the cyclic voltammetric response is a convenient means to distinguish the stepwise mechanism from a concerted one.<sup>36</sup> The simplest case is when the cyclic voltammogram becomes chemically reversible upon raising the scan rate. Indeed, as shown in Figure SIX, the simulated CVs performed in classical experimental conditions than those reported previously (ref 37) doesn't allow to discriminate between both mechanisms unless the dissociation rate of the diazenyl formed in a stepwise mechanism is lower than the values already reported for similar species.<sup>34</sup> Then, for a reduction, the presence of a reverse anodic trace is the signature of the radical or radical anion. Using ultramicroelectrodes (UME), very high scan rate can be reached, corresponding to lifetimes in the submicrosecond range for the reduced intermediate.<sup>41-43</sup> A voltammetric study was carried out on a gold ball UME with increasing scan rate in the presence of 4-NBD (Figure 1a and details in the Supporting Information). For low scan rate, no reversibility of the signal was observed. The rise of an anodic reversible voltammetric process was evidenced at a scan rate of 8080 V.s<sup>-1</sup> (Figure 1b), unambiguously demonstrating the existence of a stepwise pathway. To circumvent the electrode passivation issue possibly occurring at low scan rate and accurately estimate the diazenyl radical lifetime, the ultrafast cyclic voltammetric experiment was simulated in 1D using COMSOL Multiphysics software (V 5.5) (Table S1, Figure S1 and S2). The simulated curves for various dissociation rate constants of the species issued from the diazonium reduction at the very same scan rate are presented in the inset of Figure 1b. From the ratio of the peak intensity

$i_{\text{ox}}/i_{\text{red}}$  with  $i_{\text{ox}}$  and  $i_{\text{red}}$  corresponding to the intensity of the anodic and the cathodic peak respectively, we estimated a dissociation rate constant  $k_d$  of  $0.9 \times 10^4 \pm 0.5 \times 10^4$  s<sup>-1</sup> for the species probed experimentally (Figure S2).<sup>36</sup> This value is in good agreement with the lifetime ( $\tau = 1/k_d$ ) determined for aryldiazenyl radicals produced under pulse radiolysis and photolysis conditions (*vide supra*).<sup>34</sup>



**Figure 1.** a) Cyclic voltammetry of the 4-NBD at gold ball UME. b) Experimental and simulated (inset) cyclic voltammograms recorded at 8080 V.s<sup>-1</sup> in a 0.3 M nBu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution containing 5 mM of 4-NBD.

In a second step, we attempted to identify the aryldiazenyl radical. However, obtaining a sufficient concentration and a continuous production of the diazenyl radical allowing its characterization is challenging because the grafting process usually leads to the electrode passivation within few seconds due to the formation of multilayers.<sup>44</sup> To circumvent this issue and minimize the radical polymerization, a grafting control technique recently reported was exploited. This approach involves the use of a redox reducer activated at an electrode to induce the diazonium reduction in the diffusion layer of the electrode, as illustrated in Figure 2a.<sup>45,46</sup> Employing this strategy, the mediated diazonium electroreduction was monitored in real-time using an ultra-sensitive spectroelectrochemical bench recently developed by our group to probe electrochemically generated species in the visible range.<sup>47</sup> In this work, the dissolved atmospheric dioxygen was exploited as a redox mediator since its reduced form (superoxide anion O<sub>2</sub><sup>-</sup>) does not absorb in the wavelength range of interest. The chronoamperometric reduction of 4-NBD was monitored by absorption spectroelectrochemistry using the following potential program: 30 s at +0.5 V, followed by a 15 min electroreduction step at -0.9 V, and a 5 min final step at +0.5 V (details in the Supporting Information).



**Figure 2.** a) Mediated 4-NBD electroreduction under spectroelectrochemical monitoring, b) dynamic chronoabsorptogram recorded on GC electrode in the presence of 1 mM 4-NBD in acetonitrile  $n\text{Bu}_4\text{NPF}_6$  0.1 M. c) Experimental  $\Delta\text{Abs}_{\text{max}}$  over time (blue circles) and simulated concentration evolution of the secondary product for a dissociation constant  $k_{d,R}$  of 0 (black), 0.02 (green), 0.03 (red) and 0.04  $\text{s}^{-1}$  (yellow) obtained from 1D simulations considering a first order reaction.

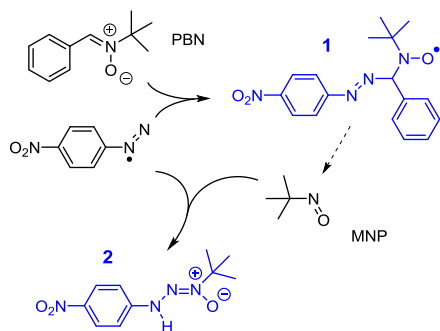
The chronoabsorptogram presented on Figure 2b shows the appearance of an absorption band  $\Delta\text{Abs}$  with a maximum located at  $\lambda_{\text{max}} \sim 450$  nm for the whole reductive step duration (*i.e.*  $-0.9$  V). The  $\Delta\text{Abs}$  value returns close to its original value when the potential is shifted to  $+0.5$  V. The absence of absorption signal after the positive potential shift confirms that the visualized absorption signal corresponds to the spectral signature of a dissolved species and not to any grafted moieties. This point was confirmed by the current-time curve presented in Figure S3, which exhibits an absence of electrode passivation. To further understand the origin of this species, the whole mechanism of the reduction process shown in Figure 2a was simulated versus time in 1D (Table S2 and Figure S4). Firstly, the theoretical concentration profile of the nitrophenyldiazenyl radical under our spectroelectrochemical analysis conditions was simulated. Using the dissociation rate constant of the diazenyl radical species  $k_d$  determined above, the simulation drives to a rapid decrease of its apparent concentration profile over

time, that is in contradiction with the quasi-constant  $\Delta\text{Abs}_{\text{max}}$  value observed in Figure 2b. While being in fair agreement with the simulated spectra obtained by TD-DFT calculation ( $\lambda_{\text{max}} \sim 500$  nm, see Figure S5), the observed absorption spectrum is thus unlikely the signature of the diazenyl radical moiety. This spectrum can neither be attributed to the nitrophenyl anion nor radical, characterized by an absorption signal in the UV domain (Figure S5). A coupling product coming from a diazenyl radical attack on the superoxide anion or the acetonitrile molecules can also be ruled out as the very same experimental spectra were obtained in DMSO or exploiting ferrocene as reducer instead of  $\text{O}_2^-$  (Figure S6).

Among the considered structures expected under electroreduction conditions (Figure S5), calculations performed for dimers resulting from nitrophenyl and/or nitrophenyldiazenyl radical couplings provide TD-DFT spectra in better agreement with the experimental one, making them good candidates for the spectroelectrochemically detected transient. A close examination of the non-accumulating process observed for this species (*i.e.* quasi-constant  $\Delta\text{Abs}$  value for the reduction step) agrees with its progressive disappearance with time as shown from the simulations of its concentration (Figures S7 and S8), considering, as a first approach, a first order dissociation rate constant  $k_{d,R}$  (Figure 2c). Noteworthy,  $k_{d,R}$  value extracted here ( $k_{d,R} = 0.03 \pm 0.01 \text{ s}^{-1}$ ) that reflects the decomposition rate of the species is also in good agreement with the decay rate of  $\Delta\text{Abs}_{\text{max}}$  once the potential is shifted to  $+0.5$  V as shown in Figure S9. This result, coupled to the large FWHM observed experimentally, suggests that spectroelectrochemical spectra might be attributed to several coupling intermediate species. Even if at that point our measurement cannot fully establish the species detected, it reveals that mediated electroreduction is an interesting pathway to continuously produce intermediate species in solution while preserving the integrity of the electrode surface.

To confirm the existence of the reactive diazenyl radical, we speculated that it should be possible to form and isolate a stable compound by radical trapping. To this end, N-terbutyl- $\alpha$ -phenylnitron (PBN), that is widely used as a radical scavenger in chemical and biological studies, was employed.<sup>48</sup> Typically, in the presence of free radicals, PBN undergoes a coupling on the benzylic  $\text{sp}^2$  carbon, giving rise to a stable nitroxyl radical derivative. PBN adducts can also lead to a spontaneous decomposition to form 2-methyl-2-nitrosopropane (MNP), also known as an efficient radical scavenger.<sup>49</sup> In order to obtain a sufficient amount of coupling product, the sustainable production of radicals was ensured by exploiting the mediated diazonium electroreduction strategy described in Figure 2a on a large area glassy carbon electrode. In a cell containing 2 mM of 4-NBD and 10 mM of PBN, a potential of  $-0.9$  V was imposed to a  $1 \text{ cm}^2$  glassy carbon electrode for 20 minutes. After electrolysis, the bulk was purified in order to selectively probe the diazenyl, leading to the detection of two main products, one of which was isolated (details in the Supporting In-

formation). The structure of compound **1** was deduced from a mass spectrometry analysis (Figure S10) and corresponds to the expected coupling product between the nitrophenyldiazenyl radical and the radical scavenger PBN (Figure 3).



**Figure 3.** Radical trapping of the nitrophenyldiazenyl radical by the PBN scavenger, followed by the decomposition of the PBN adduct **1** into MNP scavenger, leading to the MNP adduct **2**. Structure of **1** was deduced from mass spectrometry and structure of **2** was resolved by X-ray diffraction.

The structure of the second product (compound **2**, Figure 3), isolated as orange crystals, was resolved by X-ray diffraction (Supporting Information). The zwitterionic structure corresponds to the coupling of the 4-nitrophenyldiazenyl radical with the 2-methyl-2-nitrosopropane (MNP). The existence of compounds **1** and **2** unambiguously demonstrates that a diazenyl radical intermediate is produced subsequently to the 4-NBD reduction as suggested from the cyclic voltammetry experiments.

The results presented in this work shed new light on the diazonium electroreduction pathway and force us to reconsider the commonly admitted concerted mechanism. In the context of surface modification by diazonium electrografting, the existence of the diazenyl radical could have a direct impact on the film structuration. Indeed, the direct coupling of this intermediate on the surface, if demonstrated, could be responsible for the presence of azo bridges usually identified in the nanometric films and play a major role in the structure/properties relationships understanding.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details for electrode treatment, ultrafast cyclic voltammetry, spectroelectrochemistry, radical scavenging and X-ray diffraction ; Cyclic voltammetry simulations ; Spectroelectrochemistry current-time curves ; Spectroelectrochemistry simulations ; DFT calculations and TD-DFT simulated spectra; Spectroelectrochemistry control experiments ; LDI mass spectra. Crystallographic data for the compound **2** have been deposited with the Cambridge Crystallographic Data Centre with the deposition number CCDC

2151044. These data can be obtained free of charge from CCDC, [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

## AUTHOR INFORMATION

### Corresponding Author

Tony Breton – [tony.breton@univ-angers.fr](mailto:tony.breton@univ-angers.fr)  
Christelle Gautier – [christelle.gautier@univ-angers.fr](mailto:christelle.gautier@univ-angers.fr)

### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡These authors contributed equally. (match statement to author names with a symbol)

## ACKNOWLEDGMENT

The authors thank MATRIX SFR of the University of Angers and more precisely the ASTRAL and CRISTAL platforms for the characterization of organic compounds and X-ray diffraction analysis. This work was supported by the “Centre National de la Recherche Scientifique” (CNRS France) and the “Agence Nationale de la Recherche” (ANR France).

## ABBREVIATIONS

ESR, Electron Spin Resonance; CIDNP, Chemically Induced Dynamic Nuclear Polarization ; LDI, Laser Desorption Ionisation; FWHM, Full Width at Half Maximum.

## REFERENCES

- 1 M. Delamar, R. Hitmi, J. Pinson and J. M. Saveant, *J. Am. Chem. Soc.*, 1992, **114**, 5883–5884.
- 2 P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 201–207.
- 3 J. Pinson and F. Podvorica, *Chem. Soc. Rev.*, 2005, **34**, 429.
- 4 D. Belanger and J. Pinson, *Chemical Society Reviews*, 2011, **40**, 3995–4048.
- 5 A. Mesnage, X. Lefèvre, P. Jégou, G. Deniau and S. Palacin, *Langmuir*, 2012, **28**, 11767–11778.
- 6 T. Wu, C. M. Fitchett, P. A. Brooksby and A. J. Downard, *ACS Appl. Mater. Interfaces*, 2021, **13**, 11545–11570.
- 7 J. Greenwood, T. H. Phan, Y. Fujita, Z. Li, O. Ivasenko, W. Vanderlinden, H. Van Gorp, W. Frederickx, G. Lu, K. Tahara, Y. Tobe, H. Uji-i, S. F. L. Mertens and S. De Feyter, *ACS Nano*, 2015, **9**, 5520–5535.
- 8 C. Gautier, I. López and T. Breton, *Mater. Adv.*, 2021, 10.1039/D1MA00077B.
- 9 S. Baranton and D. Bélanger, *J. Phys. Chem. B*, 2005, **109**, 24401–24410.
- 10 S. S. C. Yu, E. S. Q. Tan, R. T. Jane and A. J. Downard, *Langmuir*, 2007, **23**, 11074–11082.
- 11 T. Menanteau, E. Levillain, A. J. Downard and T. Breton, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13137–13142.

- 12 A. Ghorbal, F. Grisotto, M. Laudé, J. Charlier and S. Palacin, *Journal of Colloid and Interface Science*, 2008, **328**, 308–313.
- 13 A. Adenier, E. Cabet-Deliry, A. Chaussé, S. Griveau, F. Mercier, J. Pinson and C. Vautrin-UI, *Chem. Mater.*, 2005, **17**, 491–501.
- 14 P. Doppelt, G. Hallais, J. Pinson, F. Podvorica and S. Verneyre, *Chem. Mater.*, 2007, **19**, 4570–4575.
- 15 S. Betelu, I. Tijunelyte, L. Boubekeur-Lecaque, I. Ignatiadis, J. Ibrahim, S. Gaboreau, C. Berho, T. Toury, E. Guenin, N. Lidgi-Guigui, N. Félijd, E. Rinnert and M. L. de la Chapelle, *J. Phys. Chem. C*, 2016, **120**, 18158–18166.
- 16 M. L. Usrey, E. S. Lippmann and M. S. Strano, *J. Am. Chem. Soc.*, 2005, **127**, 16129–16135.
- 17 J. Lehr, B. E. Williamson and A. J. Downard, *J. Phys. Chem. C*, 2011, **115**, 6629–6634.
- 18 T. Menanteau, M. Dias, E. Levillain, A. J. Downard and T. Breton, *J. Phys. Chem. C*, 2016, **120**, 4423–4429.
- 19 E. Atkinson, H. Warren, P. Abell and R. Wing, *Journal of the American Chemical Society*, 1950.
- 20 J. K. Kochi, *J. Am. Chem. Soc.*, 1955, **77**, 3208–3211.
- 21 R. M. Elofson, *Can. J. Chem.*, 1958, **36**, 1207–1210.
- 22 R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 1969, **34**, 854–857.
- 23 N. A. Porter, M. E. Landis and L. J. Marnett, *J. Am. Chem. Soc.*, 1971, **93**, 795–796.
- 24 R. J. Crawford and K. Takagi, *J. Am. Chem. Soc.*, 1972, **94**, 7406–7416.
- 25 N. A. Porter, L. J. Marnett, C. H. Lochmueller, G. L. Closs and M. Shobataki, *J. Am. Chem. Soc.*, 1972, **94**, 3664–3665.
- 26 L. J. Marnett, P. Smith and N. A. Porter, *Tetrahedron Letters*, 1973, **14**, 1081–1084.
- 27 J. Bargon and K.-G. Seifert, *Tetrahedron Letters*, 1974, **15**, 2265–2268.
- 28 N. A. Porter and J. G. Green, *Tetrahedron Letters*, 1975, **16**, 2667–2670.
- 29 N. A. Porter, G. R. Dubay and J. G. Green, *J. Am. Chem. Soc.*, 1978, **100**, 920–925.
- 30 O. Brede, R. Mehnert, W. Naumann and H. G. O. Becker, *Berichte der Bunsengesellschaft für physikalische Chemie*, 1980, **84**, 666–672.
- 31 T. Suehiro, S. Masuda, T. Tashiro, R. Nakauza, M. Tagushi, A. Koike and A. Rieker, *Journal of the American Chemical Society*, 1986.
- 32 J. Stephen. Adams, K. A. Burton, B. Kim. Andrews, R. Bruce. Weisman and P. S. Engel, *J. Am. Chem. Soc.*, 1986, **108**, 7935–7938.
- 33 T. Suehiro, S. Masuda, T. Nakauza, M. Taguchi, A. Mori, A. Koike and M. Date, *Bulletin of the Chemical Society of Japan*, 1987.
- 34 C. Galli, *Chem. Rev.*, 1988, **88**, 765–792.
- 35 L. Pause, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 1999, **121**, 7158–7159.
- 36 J.-M. Savéant, Academic Press, 2000, vol. 35, pp. 117–192.
- 37 C. P. Andrieux and J. Pinson, *J. Am. Chem. Soc.*, 2003, **125**, 14801–14806.
- 38 A. Mesnage, S. Esnouf, P. Jégou, G. Deniau and S. Palacin, *Chem. Mater.*, 2010, **22**, 6229–6239.
- 39 B. Ortiz, C. Saby, G. Y. Champagne and D. Bélanger, *Journal of Electroanalytical Chemistry*, 1998, **455**, 75–81.
- 40 M. Ceccato, L. T. Nielsen, J. Iruthayaraj, M. Hinge, S. U. Pedersen and K. Daasbjerg, 2010, 10.
- 41 C. Amatore, E. Maisonhaute, B. Schöllhorn and J. Wadhawan, *ChemPhysChem*, 2007, **8**, 1321–1329.
- 42 X.-S. Zhou, B.-W. Mao, C. Amatore, R. G. Compton, J.-L. Marignier, M. Mostafavi, J.-F. Nierengarten and E. Maisonhaute, *Chem. Commun.*, 2016, **52**, 251–263.
- 43 C. Amatore, E. Maisonhaute and G. Simonneau, *Journal of Electroanalytical Chemistry*, 2000, **486**, 141–155.
- 44 A. Adenier, C. Combellas, F. Kanoufi, J. Pinson and F. I. Podvorica, *Chem. Mater.*, 2006, **18**, 2021–2029.
- 45 L. Pichereau, I. López, M. Cesbron, S. Dabos-Seignon, C. Gautier and T. Breton, *Chem. Commun.*, 2019, **55**, 455–457.
- 46 I. López, S. Dabos-Seignon and T. Breton, *Langmuir*, 2019, **35**, 11048–11055.
- 47 O. Alévêque, C. Gautier and E. Levillain, *Current Opinion in Electrochemistry*, 2019, **15**, 34–41.
- 48 D. N. Polovyanenko, V. F. Plyusnin, V. A. Reznikov, V. V. Khramtsov and E. G. Bagryanskaya, *J. Phys. Chem. B*, 2008, **112**, 4841–4847.
- 49 D. W. H. Merckx, L. Plankensteiner, Y. Yu, P. A. Wierenga, M. Hennebelle and J. P. M. Van Duynhoven, *Food Chemistry*, 2021, **334**, 127578.

Insert Table of Contents artwork here

