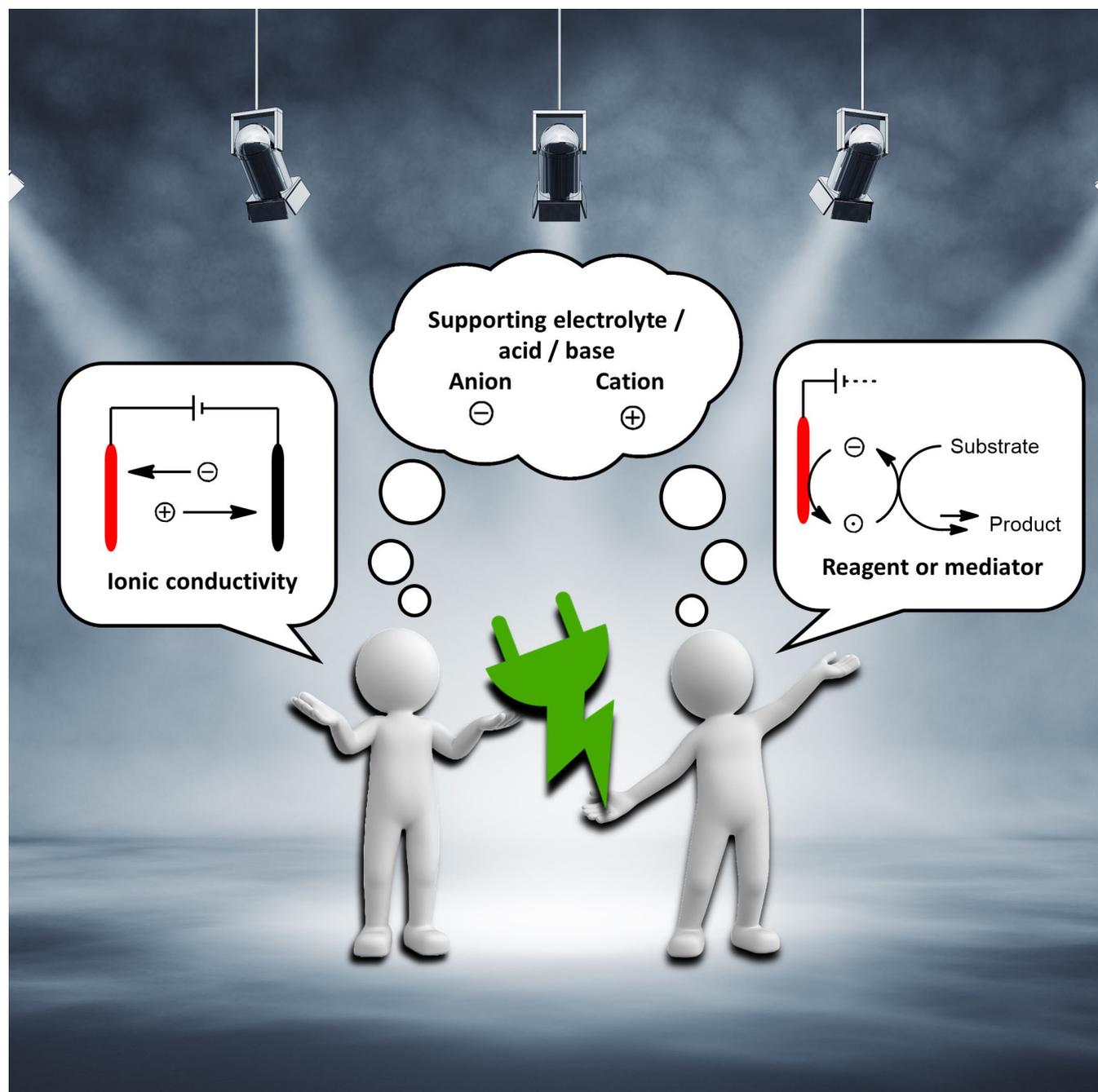


Dual Roles of Supporting Electrolytes in Organic Electrosynthesis

Lilla G. Gombos^{+, [a]}, Joachim Nikl^{+, [a]} and Siegfried R. Waldvogel^{*, [a, b, c]}



Synthetic electro-organic chemistry is advancing to a well-established methodology in academic research and industry. The simple process control minimizes reagent waste and avoids using toxic and environmentally unfriendly redox agents, providing a feasible and sustainable alternative to conventional techniques. However, a fundamental disadvantage, is the necessity of ion-conductive components within the electrolyte. The recovery of these supporting electrolytes, as well as simple product isolation, pose challenges for work-up strategies. This

review presents the following electrochemical protocols featuring a simple material- and resource-saving strategy: the dual role of supporting electrolytes as conductivity enabling components and reagents or mediators. This review is the first to conclude and categorize dual role strategies for the supporting electrolytes. It may inspire electrochemists to advance the development and optimization of electrochemical synthesis protocols towards more material- and resource-efficient reaction control.

1. Introduction

Resource efficiency and waste prevention have become more and more critical in chemical production since the end of the last century, shifting the focus from production yield to applying sustainable approaches and waste-minimizing reaction conditions. In 1992, R. A. Sheldon introduced the environmental factor (E factor) that shed light to the tremendous waste problem in the chemical industry. His calculations showed that depending on the industrial segment, up to 5 kg waste/kg product for bulk chemicals, 50 kg waste/kg product for fine chemicals, and > 100 kg waste/kg product for pharmaceuticals are produced annually.^[1] Therefore, it is crucial to design and develop chemical synthesis routes that optimize waste-preventing measurements.

An important benchmark for assessing the sustainability of a synthesis is its atomic economy, first defined by B. M. Trost in 1991 as the percentage ratio between the mass of the desired product and the total mass of all products.^[2] Atomic economy is an essential criterion of the green chemistry concept. Its principles were developed by Paul Anastas and John Warner in the 1990s to improve chemical synthesis.^[3] To achieve a good atom economy for a reaction, the incorporated number of atoms must be augmented into the desired product to minimize waste. Furthermore, no additives, co-solvents, or similar should be used to minimize the overall material input of chemicals. A fundamental component of organic electrolysis is the electrolyte, consisting of a solvent (mixture) and a preferable

chemically inert salt (supporting electrolyte), which ensures the electrical conductivity of the reaction medium.

For a long time, the role of the supporting electrolyte was underestimated to be a solely ionic conductor, contributing to improved mass transfer and, hence, providing precise and stable electrochemical conditions. Unlike mediators or substrates, this salt should not have an electroactive role during electrolysis.^[4]

Mediated electrochemistry methodologies enhancing the concept of selective electro-organic synthesis were introduced in the second half of the 20th century.^[5] The mediator represents a redox electroactive species that is easily oxidized or reduced at the electrode surface due to its beneficial redox potential and promotes the reactivity of interest as it further reacts with the substrate. This catalytic effect provides a narrowed and highly selective electrochemical window that provides the desired compounds with excellent yields and selectivity under the right conditions. Ideally, the mediator should be recycled as part of the electrocatalytic cycle, maintaining the conductivity of the reaction and lowering waste. These advantages led to considerable attention in introducing the idea of a “supporting electrolyte-free” methodology. This changes the view of the supporting electrolyte as an entity, now urged to be used in a dual role as a reagent or a mediator.

For enabling sufficient conductivity, many examples employ protic solvent mixtures or over-stoichiometric amounts of salts, compromising the meaning of the “supporting electrolyte-free” concept and green chemistry principles.

To describe the methodology of electro-organic synthesis in a material-efficient and resource-saving direction, various concepts for the dual-role-electrolytes were categorized and will be outlined in this review. For clarity, the electrolyte anions and cations were distinguished and treated separately in their roles, enabling the characterization of anodic and cathodic processes, including the respective ions. Furthermore, the reactant or mediator role of the supporting electrolyte is demonstrated based on the proposed mechanisms in the original publications. After carefully reviewing the literature, the following criteria were defined to assist in the classification of the respective synthesis protocols:

- 1.) Only a single salt (or one Brønsted–Lowry acid) is used in the electrolyte. In-situ formation of electrolyte ions by acid-base reactions are considered.
- 2.) Dual catalytic cycles, e.g., involving an additional organic mediator next to an electrocatalytically active supporting electrolyte's anion or cation, are disregarded.

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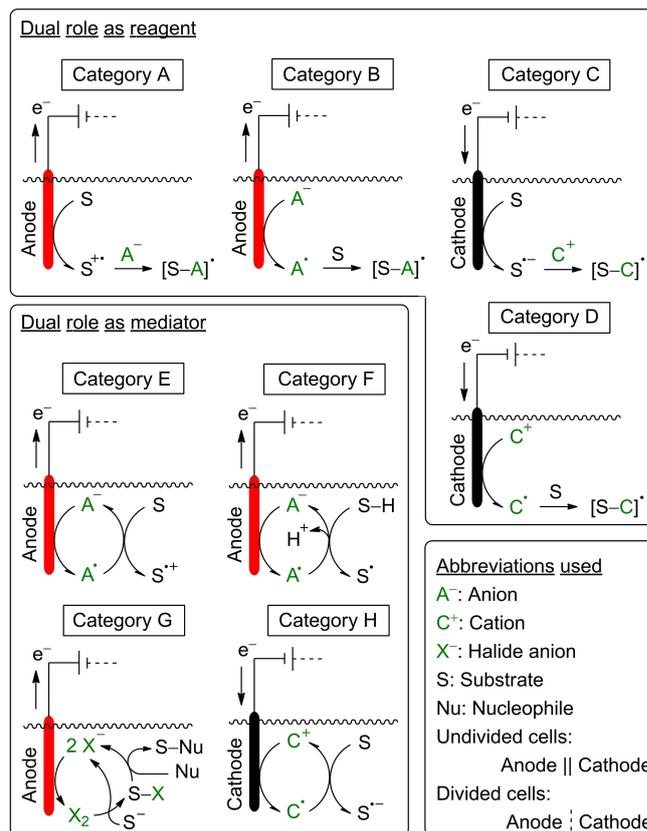
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Protocols matching the set criteria were sorted into eight categories (A–H). Scheme 1 presents these categories, including detailed mechanistic deliberations to assist the reader in better understanding our choices. The categories were distinguished between anodic and cathodic processes, as well as the dual role purpose of the respective ion as a reagent or a mediator. Wherever an electrochemical method with an unmistakable dual role of the supporting electrolyte could not fit the above criteria, it was presented in a “Miscellaneous” section following the individual categories.

2. Dual role as a reagent

This section defined four categories to classify the electrolyte's dual role as a reagent mechanistically. Depending on the redox reactivity, the electrolyte can be oxidized or reduced at the electrode surface as the first step or take a secondary role in the reaction mechanism. Category A refers to the electrolyte's anion as a scavenging reagent towards an oxidized substrate intermediate. Here, the anodic oxidation of the substrate is favored over the anion, with the latter forming a nucleophilic bond with the intermediate. Category B refers to the preferential oxidation of the anion over the substrate. The substrate then scavenges the highly reactive intermediate or radical species via a nucleophilic attack. Category C describes a reductive process of the substrate that subsequently attacks the electrolyte cation. A reverse case is the preferential reduction of the cation over the substrate, whereby the substrate attacks the radical formed (category D).



Scheme 1. Definition of the categories regarding the supporting electrolyte's mechanistic dual role purpose.



Lilla G. Gombos received her MSci degree in Pharmaceutical Chemistry working on the aza-Claisen rearrangement of vinylaziridines with in-situ generated arynes under the supervision of Dr. Christopher R. Jones at Queen Mary University of London. During a RISE DAAD Scholarship she was working in the group of Prof. Dr. S. R. Waldvogel on electrochemical cross-coupling reactions. Most recently, she has been working on her Ph.D. project regarding electrochemical bromine generation for direct and mediated organic synthesis under the supervision of Prof. Dr. S. R. Waldvogel at Johannes Gutenberg University Mainz.



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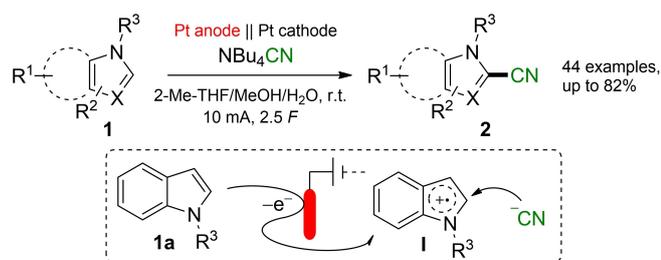
2.1. Category A (substrate oxidation prior to anion)

The most common example concerning an electrolyte's dual role is using the anion as a nucleophilic reagent that reacts with a previously oxidized substrate. For clarity reasons, carbon-carbon and carbon-heteroatom bond formations are described separately. In terms of a C–C bond formation, a recent procedure describes the cyanation of *N*-heterocycles using tetrabutylammonium cyanide as electrolyte and reagent (Scheme 2).^[6] Indoles, pyrroles, imidazoles, and pyrazoles are functionalized in a rather exotic 5:2:0.1 mixture of 2-methyltetrahydrofuran, methanol, and water solvent system showing large functional group tolerance. The respective *N*-heterocycles **1** are oxidized in the presence of 2.5 eq. NBu_4CN to form the desired products **2** in a highly selective fashion. This robust and scalable method was extended to the selective cyanation of aza-indoles in batch and flow synthesis, furnishing more than 50 examples with up to 82% yield.

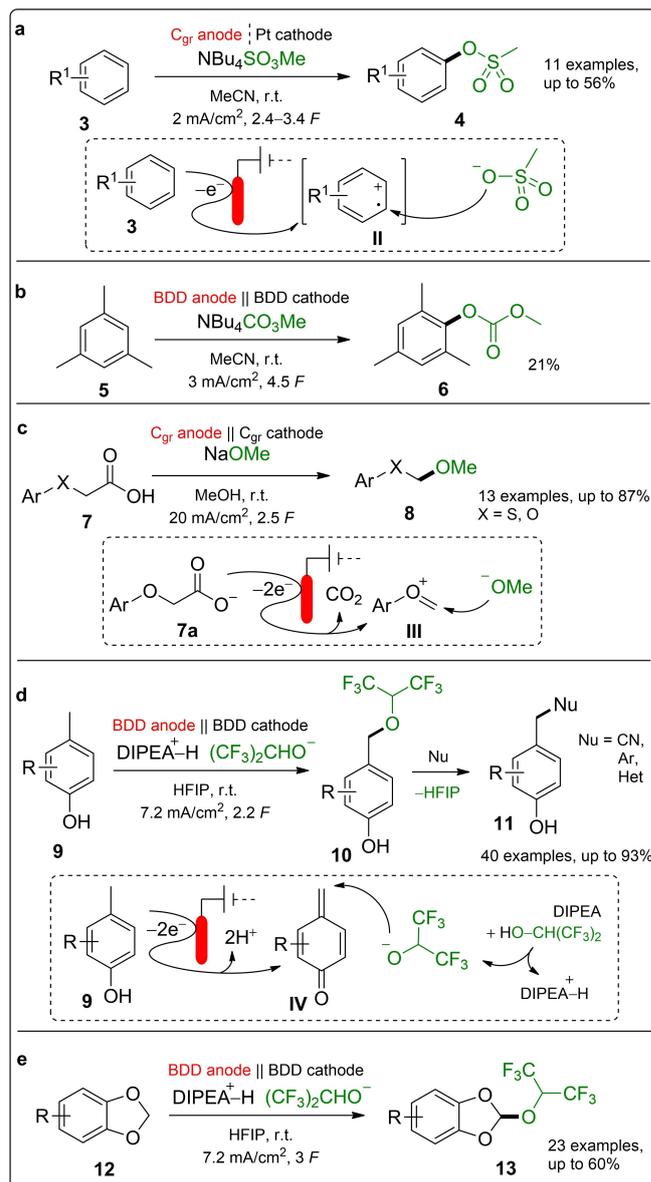
Extensive research has been performed in the Waldvogel group tackling C–O bond formation while using supporting electrolytes in a dual role. The first direct dehydrogenative anodic mesylation of aromatic compounds was described in 2019, using tetrabutylammonium methanesulfonate in acetonitrile as an electrolyte (Scheme 3a).^[7] The reaction worked best with isostatic graphite anodes in a divided cell using a glass frit separator. Analogous to the previous example, the sulfonate anions attack the electrochemically oxidized substrates, providing the aryl mesylate products **4** with 11 examples and up to 56% yield.

A similar protocol leads to the direct electrochemical formation of aryl alkyl carbonates (Scheme 3b).^[8] Here, tetrabutylammonium monomethyl carbonate is used as a supporting electrolyte to form the corresponding mesityl methyl carbonate **6** with a 21% yield. The solvent and electrode material choice promotes selective C–H activation, which is crucial for this protocol's success. In addition, the interelectrode gap turned out to be pivotal, which is an often-underestimated parameter.^[9]

Based on the research of Schäfer (1993) and Lam (2018),^[10] an electrochemical decarboxylative synthesis protocol for aryl methoxymethyl ether (MOM) was developed (Scheme 3c).^[11] Aryloxymethylcarboxylates are formed in-situ using equimolar NaOMe in methanol to create the necessary conductivity for the reaction medium. Subsequently, after anodic oxidation and decarboxylation, the forming oxonium intermediate **III** is



Scheme 2. Electrochemical cyanation of *N*-heterocycles using NBu_4CN as a cyanide source.^[6]



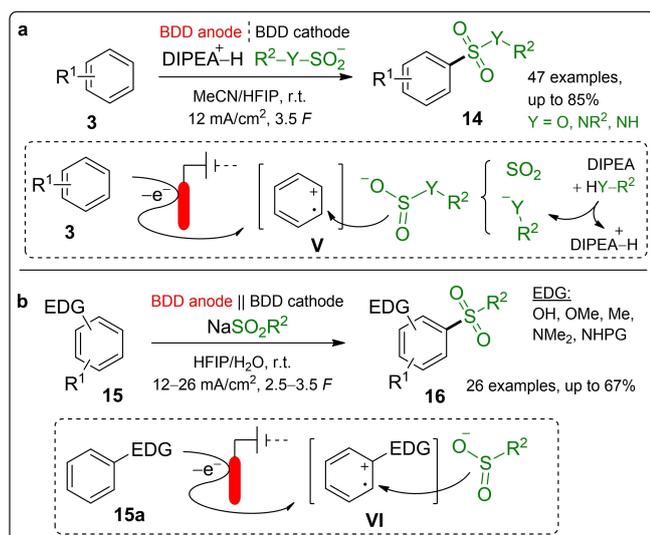
Scheme 3. Electrochemical C–O bond formation using various electrolyte compositions. **a** Aryl mesylate synthesis using $\text{NBu}_4\text{SO}_3\text{Me}$ in a dual role.^[7] **b** Generation of aryl alkyl carbonates by dehydrogenative coupling.^[8] **c** Decarboxylative aryl methoxymethyl ether synthesis using sodium methoxide.^[11] **d** Benzylic HFIP ether formation^[12] and **e** orthoester formation^[15] using HFIP/amine mixtures as electrolyte.

attacked by methoxide anions to form the desired products. Compared to the previous examples, this decarboxylative methoxylation procedure provides the corresponding MOMs **8** with up to 70% current efficiency, avoiding carcinogenic MOMCl.

A series of benzylic coupling reactions of phenols with various nucleophiles have been investigated following the strategy of precedent 1,1,1,3,3,3-hexafluoroopropan-2-ol (HFIP) ether formation (Scheme 3d).^[12] An innovative electrolyte combination of HFIP and tertiary amines, like *N,N*-diisopropylethylamine (DIPEA), provides enough ionic conductivity and hosts the HFIP anion as a potential nucleophilic reagent.^[13]

Furthermore, due to the electrolyte's low boiling point, it can be fully recovered by distillation.^[14] After the two-fold oxidation of the electron-rich phenol **9**, the quinone-like intermediate **IV** is attacked by the in-situ formed HFIP-propanoate, creating the desired C–O bond. Several nucleophiles can be used for further functionalization reactions, demonstrated with an overall 40 examples and excellent yields with up to 93% (Scheme 3d). Following these examples, the same methodology provides the formation of fluorinated orthoesters **13** from 1,3-benzodioxoles **12** (Scheme 3e).^[15]

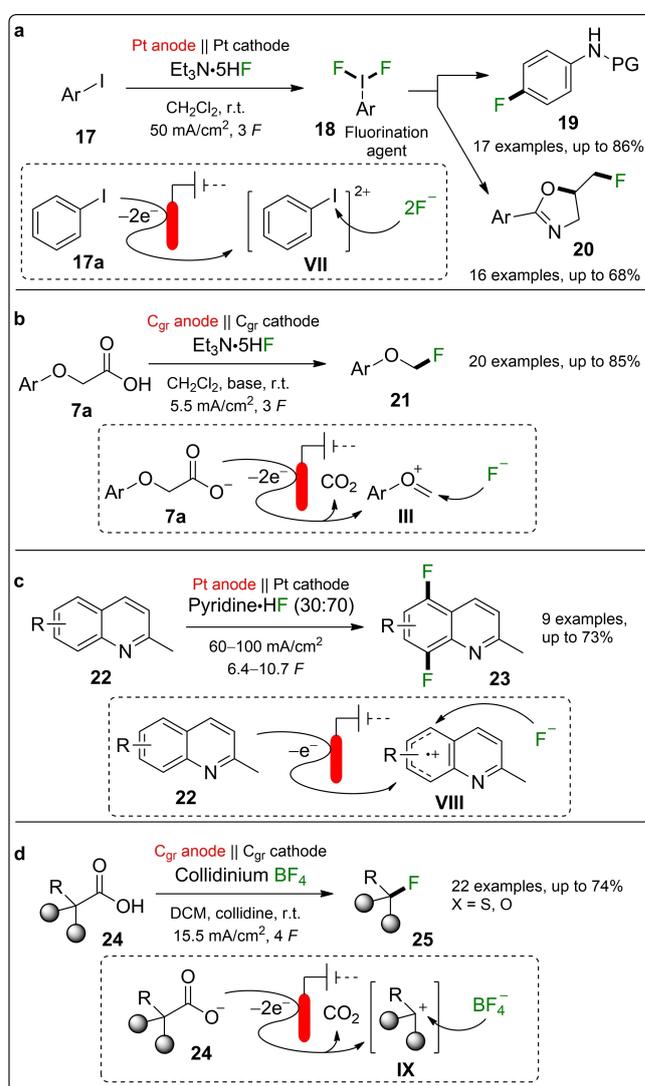
Electrochemical C–S bond formations can be forged with the participation of sulfur-containing electrolyte anions. For example, in-situ generated sulfite or sulfinate anions are excellent choices. A widely applicable, unique protocol allows the in-situ formation of ion-conducting supporting electrolytes using an SO₂ stock solution. The addition of either amines or alcohols and subsequent deprotonation leads to the corresponding amidosulfonates or monoalkyl sulfites, scavenging electrochemically oxidized electron-rich aromatics without the necessary pre-functionalization steps (Scheme 4a). Via this multi-component reaction,^[16] sulfonamides^[17] as well as alkyl arylsulfonates^[18] with yields up to 80% could be achieved. The electrochemical transformation is very effective, providing the ability to be performed under scalable, continuous flow conditions in an undivided set-up.^[19] Such approaches are particularly interesting since a cost-driving work-up procedure is facilitated.^[20] Apart from the in-situ generated supporting electrolytes, bench-stable sulfinate salts proved an adequate choice in electrochemical C–S coupling reactions. While the electrochemical sulfonylation of electron-rich aromatics has been demonstrated in a couple of examples, only the sulfinate salts were applied in a dual role (Scheme 4b).^[21] The simple set-up and a low excess of 1.3 eq. sulfinate salt fosters this attractive protocol in a material-saving manner. The unique



Scheme 4. Electrochemical C–S bond formation of electron-rich aromatics. **a** Sulfonamide and Aryl alkylsulfonate synthesis via a multi-component reaction and in-situ generated supporting electrolyte.^[17,18] **b** Sulfonylation using sodium sulfonates in a dual role.^[21]

choice of solvent and robust, carbon-based electrodes ensures the selectivity of this approach and provides the coveted products **16** with yields up to 67%.

Electrochemical fluorination reactions are carried out frequently using amine-stabilized hydrofluoric acids. Partial protonation of the amine and formation of fluoride anions provide the mandatory conductive medium, making additional use of supporting electrolytes unnecessary. In various applications, this fluoride anion is a scavenger for anodically oxidized substrates, constituting a mild way to form C–F bonds in a sustainable way. In-situ formation of fluorinated hypervalent iodoarene species can promote mild reaction pathways for fluorinating aniline derivatives or building fluorinated heterocycles (Scheme 5a). The depicted protocols use triethylamine pentahydrofluoride. By activating the anilide nitrogen, the fluorination is selectively directed in the *para* position, reaching



Scheme 5. Electrochemical C–F bond formation reactions of different substrates. **a** Formation of fluorinated hypervalent iodoarene species as reactive agents for different substrate fluorinations.^[22,23] **b** Fluorodecarboxylation to form fluoromethyl aryl ethers.^[24] **c** Regioselective difluorination of quinolines using the Olah reagent.^[26] **d** Fluorodecarboxylation to form tertiary alkyl fluorides using tetrafluoroborate as fluoride source.^[30]

yields up to 86%.^[22] Employing *N*-allyl carboxamides, an electrochemical fluorocyclization could be achieved under the same reaction conditions, forming 2-oxazolines **20** with yields up to 68%.^[23]

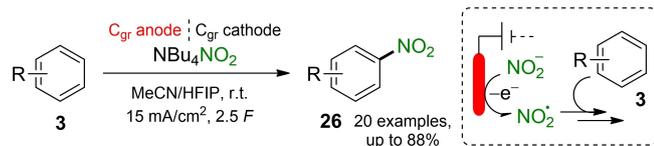
A different approach under comparable conditions was used for a fluorodecarboxylation of aryloxyacetic acids to form fluoromethyl aryl ethers **21** with yields up to 85% (Scheme 5b).^[24] Here, a base is used to enhance the substrate's partial deprotonation and anodic oxidation. Other electrochemical fluorination protocols also utilize triethylamine hydrofluoride combinations in a dual role, highlighting its frequent application in electrochemical fluorination reactions.^[25] A regioselective difluorination of quinolines has been reported by Shaikh et al.^[26] Based on preliminary work regarding the benzylic fluorination of *p*-nitrotoluenes,^[27] the difluorination protocol employs the Olah reagent (HF:pyridine = 70:30)^[28] as a reagent and supporting electrolyte in an undivided cell setup (Scheme 5c).

The understanding of the definition of dual roles can vary. For example, utilizing ionic liquids as 'solvent-free' protocols can also provide a resource-saving approach. The amine-stabilized hydrogen fluorides, for instance, R₃N·*n*HF or R₄NF·*n*HF, have the advantage of being liquids at room temperature, providing an alternative route for solvent-free electrolysis. Fuchigami and Inagi discussed these reagents as excellent wellsprings for anodic fluorination, displaying a dual role as the fluoride ion source and the solvent.^[29]

Besides the mixtures of amines and hydrogen fluoride, an electrochemical fluorination protocol has been described applying tetrafluoroborate anions as a fluorine source. The Lam group recently developed a protocol for decarboxylative fluorination of various tertiary carboxylic acids to tertiary alkyl fluorides **25** were obtained with good yields.

2.2. Category B (anion oxidation prior to substrate)

Category B describes the first-step anodic oxidation of the anions to an electrophilic entity that triggers the reaction of interest (Scheme 1). A nitration protocol of electron-rich aromatics like phenols, anilines, and arenes has been described as an example of C–N bond formation. Here, 3.0 eq. tetrabutylammonium nitrite is used in a dual role as a reagent (Scheme 6). The nitrite anion is anodically oxidized to nitrogen dioxide/dinitrogen tetroxide, forming an arene-NO⁺ complex

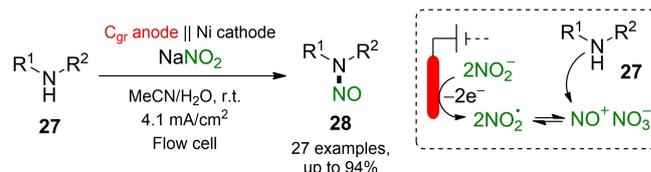


Scheme 6. Electrochemical nitration of electron-rich arenes using NBu₄NO₂ as nitration reagent.^[31]

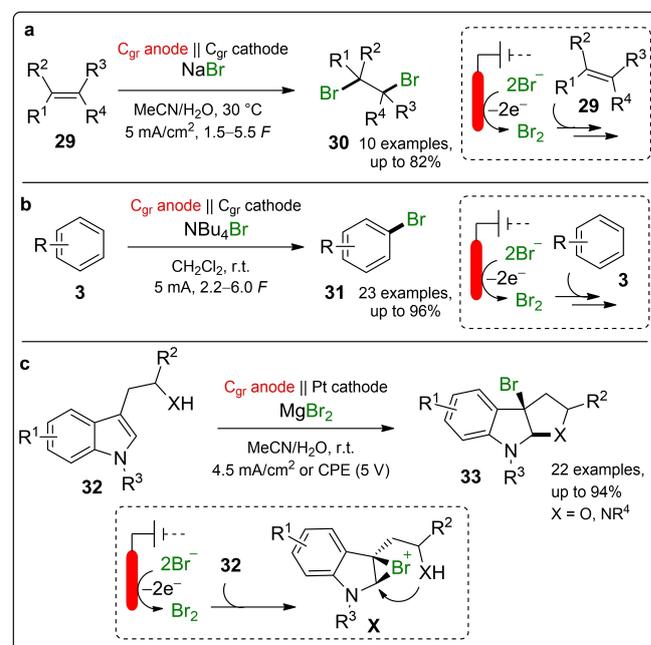
responsible for the nitration step.^[31] Stoichiometric amounts of HFIP promote the reaction to provide 20 examples with up to 88% yield.

Staying in the range of nitration reactions, the Wirth group recently published a protocol for the nitration of amines, fostering an N–N bond formation in flow. In contrast to the previously described protocol, sodium nitrite serves a dual role (Scheme 7). Via the anodic nitrite oxidation, an electrophilic NO⁺NO₃⁻ complex is formed that triggers a nucleophilic attack of the respective amine. The protocol describes 27 *N*-nitrosamines **28** with excellent yields of up to 94%.^[32]

Many protocols that match the criteria of category B derive from the anodic oxidation of halide anions, most commonly bromide or iodide. Example protocols are shown in Scheme 8. The selective dibromination of delicate terpenes and naturally derived olefins using simple sodium bromide as a supporting electrolyte and bromination agent was described in our group (Scheme 8a). Upon oxidation of the bromide anions to form a bromine/tribromide equilibrium, the bromine reacts with the alkene double bond to form the dibrominated species yielding



Scheme 7. Electrochemical nitration of amines using NaNO₂ as nitrosylation reagent in flow.^[32]



Scheme 8. Electrochemical C–Br bond formation using bromide salts in a dual role. **a** Dibromination of naturally occurring alkenes with sodium bromide.^[33] **b** Bromination of different aromatics using tetrabutylammonium bromide.^[34] **c** Bromo cyclization using magnesium bromide.^[35]

up to 82%.^[33] This electrochemical approach proved to be superior in selectivity towards conventional methods.

A similar bromination procedure of aniline derivatives, indoles, and pyridines was described by Xiang et al. utilizing tetrabutylammonium bromide in a dual role (Scheme 8b). This method proved to have a high functional group tolerance, allowing the selective *p*-brominate products **31**.^[34]

An example of a bromocyclization reaction has been reported from the Vincent group, using magnesium bromide in a dual role as an electrolyte and bromination agent (Scheme 8c).^[35] The protocol describes the conversion of tryptophol, tryptamine, and tryptophan derivatives to 3a-bromofuranoindolines and 3a-bromopyrroloindolines **33**, which are fundamental intermediates in natural product synthesis. This process proved equally efficient under constant potential and current electrolysis without additional supporting electrolyte salts.

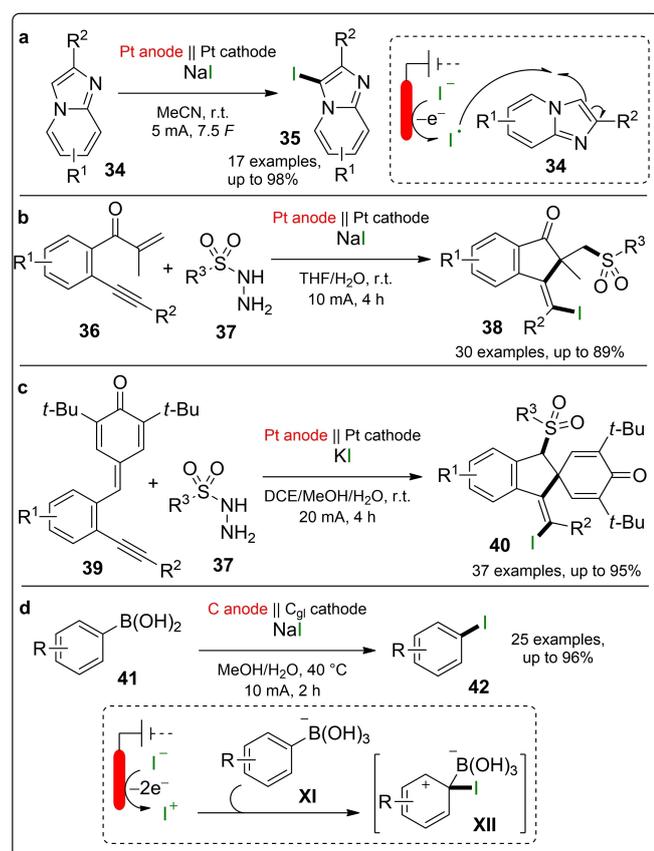
In addition to that, the iodination of heteroaromatics was described by Kim et al. Simple sodium iodide acts as the supporting electrolyte while the iodide anions are oxidized to its radicals at the platinum anode (Scheme 9a). The representing imidazo[1,2-*a*]pyridines **34** are iodinated in 3-position following a radical pathway, depicting important intermediates in pharmaceuticals and biologically active compounds.^[36] A

similar protocol using tetrabutylammonium bromide/chloride salts at carbon-based electrodes was published one year later, providing the corresponding halogenated substrates.^[37]

The Jiang group demonstrated two examples of electrochemical, iodine radical-induced cascade cyclization reactions (Scheme 9b and 9c). These annulation-iodosulfonylation reactions are based on using sodium or potassium iodide in a dual role and arylsulfonylhydrazines as radical coupling reagents.^[38] Furthermore, an electrochemical *ipso*-halogenation reaction has been performed using arylboronic acids and sodium iodide as a supporting electrolyte and a reagent (Scheme 9d). The literature describes an anodic oxidation of the iodide to a hypervalent I⁺ species, followed by an S_EAr₂^{ipso} reaction mechanism.^[39] The literature describes the formation of borate anions from the boronic acid substrates in aqueous media. The method tolerates a broad substrate scope, including electron-donating and -withdrawing groups.

Compared to the sulfinate salts described in category A, examples also provide insight into the mechanistic approach to oxidize these salts prior to the substrates. A protocol published by Han et al. exhibits this approach on an alkynyl/alkenyl migration-sulfonylation of double bonds (Scheme 10). Here, dual-role sodium sulfinate salts are converted to sulfonyl radicals via anodic oxidation. After radical addition to the double bond, an intramolecular migration step occurs to form **44**.^[40]

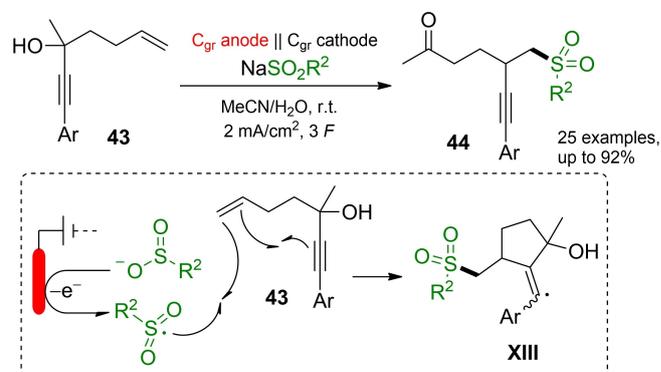
Advances in the formation of peroxodicarbonate from carbonate-based supporting electrolytes were reported. The highly reactive peroxodicarbonate solution is prepared in a continuous circular flow electrolysis, serving as an oxo-transfer reagent in subsequent ex-cell reactions to achieve the formation of *N*-oxides, epoxides, and sulfone derivatives.^[41]



Scheme 9. Electrochemical C-I bond formation using iodide salts in a dual role. **a** Iodination in 3-position of imidazo[1,2-*a*]pyridines.^[36] **b** Annulation-iodosulfonylation to form 1-indanones.^[38a] **c** Annulation-iodosulfonylation to form (*E*)-spiroindenes.^[38b] **d** *Ipso*-iodination of arylboronic acids.^[39]

2.3. Category C (substrate reduction prior to cation)

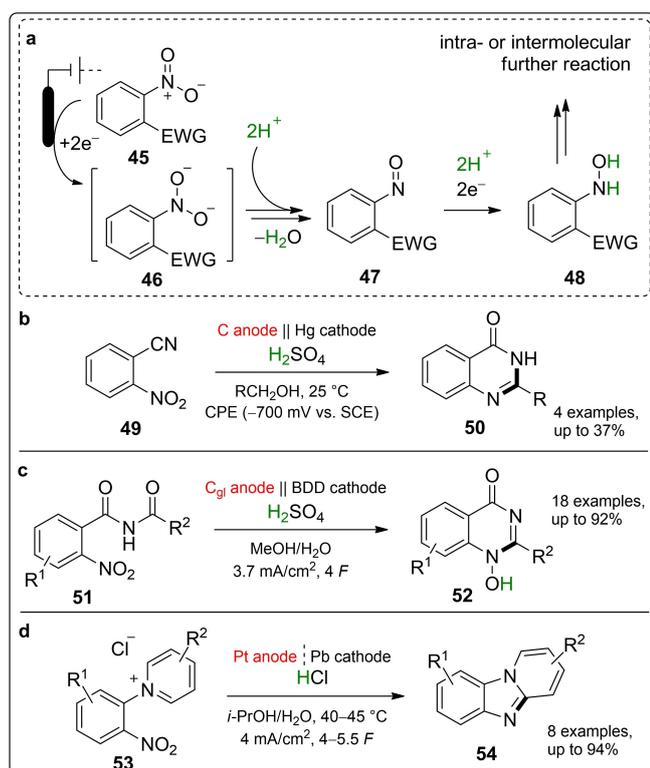
Prominent reductive conversions where the substrate is reduced prior to the supporting electrolyte's cation have already been reported in the 1980s for the cathodic dimerization of certain pyridinium salt analogs. However, these conversions were still conducted in the presence of a secondary supporting electrolyte.^[42]



Scheme 10. Electrochemical alkynyl/alkenyl migration-sulfonylation of alkenes using sodium sulfinate salts.^[40]

Today, they are especially common for hydrogenation reactions, where protic media and Brønsted–Lowry acids like HCl, H₂SO₄, provide the necessary protons and conductivity. Reduction of nitroarenes, followed by subsequent intra- or intermolecular reactions, are widespread in electrochemistry. A general mechanistic proposal is given in Scheme 11a. After the reduction and subsequent protonation, the nitro group is transformed into a nitroso group and further to a hydroxylamine functionality, which can undergo intra- or intermolecular follow-up reactions. An example of an intermolecular follow-up reaction was presented by Estrada and Rieker in 1994. Using sulfuric acid as an electrolyte, the 2-nitrobenzamide **49** suffers a reduction under constant potential electrolysis at a mercury cathode (Scheme 11b). Different alcohols serve as solvents, which were implemented in the resulting 2-alkyl-4(3*H*)-quinazolinone **50** products.^[43]

Intramolecular reactions are shown in Schemes 11c and 11d. In a protocol presented by Waldvogel et al. nitrobenzamide substrates **51** are reduced to the corresponding hydroxylamine intermediates **48** using sulfuric acid as a supporting electrolyte (Scheme 11c). Subsequently, an intramolecular condensation occurs, leading to 1*H*-1-hydroxy-quinazolin-4-ones **52** with excellent yields.^[44] A 100-fold scale-up was proven on a 15 mmol batch, revealing the robustness and scalability of this protocol.



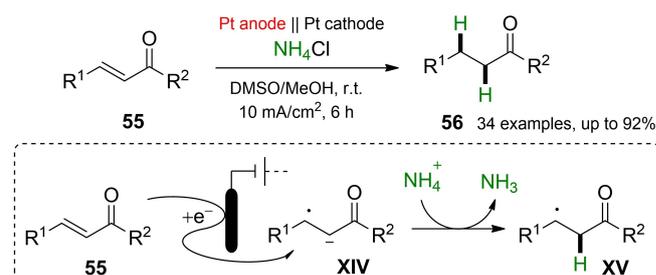
Scheme 11. Electrochemical reduction of nitro group-containing substrates by using the supporting electrolyte protons. **a** General, mechanistic scheme of the nitro group reduction. **b** Intermolecular follow-up reaction with alcohol solvent to form 2-alkyl-4(3*H*)-quinazolinones.^[43] **c** Intramolecular reaction of nitrobenzamide to 1*H*-1-hydroxy-quinazolin-4-ones.^[44] **d** Intramolecular reaction of Zincke-type salts to pyrido[1,2-*a*]benzimidazoles.^[45]

A different intramolecular cyclization reaction was reported by Gulyai et al. (Scheme 11d). Pyrido[1,2-*a*]benzimidazoles were synthesized from Zincke-type precursors.^[45] Hydrochloric acid performs as a supporting electrolyte and supplies the protons for the cathodic reduction of the nitro group.

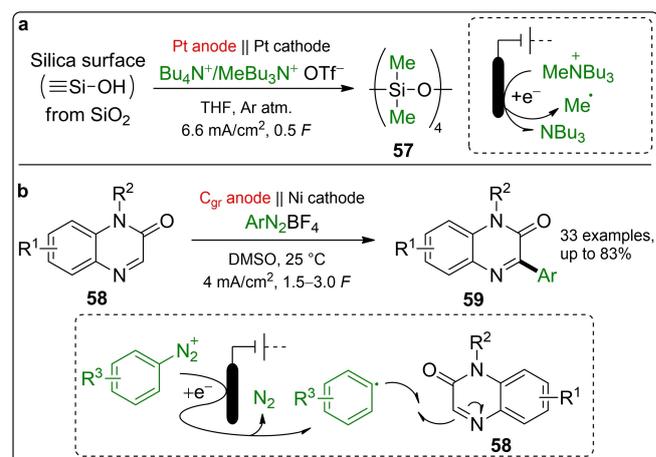
Besides the reduction of nitro groups, the selective electrochemical reduction of alkenes to alkanes has also been researched. In the presence of 4.0 eq. of ammonium chloride, Xia et al. achieved the selective hydrogenation of α,β -unsaturated **55** ketones to saturated ketones via a direct substrate reduction on a platinum cathode (Scheme 12). The proton source derives from the ammonium cation. This simple protocol provides the resulting products **56** with excellent yields of up to 92%.^[46]

2.4. Category D (cation reduction prior to substrate)

Category D describes a rather unusual and electrochemically disfavored approach. The reduction of a supporting electrolyte's cation is not often encountered in literature due to the substrate's high reduction potential. A few examples are presented in Scheme 13. The challenge of an electrochemical siloxane formation directly from glass (silica surface) has been



Scheme 12. Electrochemical hydrogenation of α,β -unsaturated ketones using ammonium chloride as supporting electrolyte and proton donor.^[46]



Scheme 13. Electrochemical reduction of the supporting electrolyte cations with subsequent reactions. **a** Formation of dimethyl siloxane rings directly from silica surface.^[47] **b** Arylation of quinoxalin-2(1*H*)-one derivatives with dual-role aryldiazonium tetrafluoroborate.^[48]

tackled (Scheme 13a). The authors claim that methyltributylammonium cation impurities in tetrabutylammonium triflate (supporting electrolyte) are responsible for the formation of methyl radicals, enabling the formation of three- to five-membered dimethyl siloxane rings.^[47]

A different case was described by Little and Zeng, performing an arylation of quinoxalin-2(1*H*)-one substrates **58** using aryldiazonium tetrafluoroborate salts (Scheme 13b). After cathodic reduction of the aryldiazonium cation and nitrogen evolution, the respective aryl radical selectively recombines with the substrate at position 3. The protocol shows a broad substrate scope with yields up to 83%.^[48]

As represented by these examples, supporting electrolytes in a dual role as reagents can offer promising sustainability features and display unique and diverse reactivities in electrochemical synthesis. In addition to that, distinctive selectivity can be demonstrated via rather peculiar reaction mechanisms. Nevertheless, when the supporting electrolyte is applied as a dual-role reagent, its consumption may cause an increase in ohmic resistance with a reduced reaction selectivity. Therefore, most protocols must compromise with an excess amount of the supporting electrolytes or a mixture of solvents to provide sufficient conductivity for the reaction media. Using the electrolyte components in a mediator role instead can offer an increased range of applications by using fewer materials simultaneously.

3. Dual role as mediator

Four categories were defined for mechanistically classifying the electrolyte's dual role as a mediator. Category E refers to the anion as a simple electron transfer catalyst, where an electron from the substrate is transferred to the oxidized radical, regenerating the anion. Category F refers to the anion's function as a hydrogen atom transfer catalyst after anodic oxidation. Here, an H atom is radically transferred from a substrate while the electrolyte anion is regenerated (PCET, proton-coupled electron transfer). The substrate radical reacts further with itself or with other electrolyte components accordingly. Category G describes a particular case of a mediator role of electrolyte anions. Here, mainly halides are summarized, which, after anodic oxidation, first form dissolved halogen molecules and reactions with the substrate. Followed by a nucleophilic substitution, the halide is regenerated. Category H, analogous to category E, is an electron transfer process where the cathodically reduced cation transfers an electron to a substrate and is revived as a cation.

3.1. Category E (anion as oxidative electron transfer mediator)

Category E focuses on rare cases where the supporting electrolyte's anion is described as an electron transfer mediator.

An example from the Waldvogel group describes a dehydrogenative cyanamidation of thioethers using tetrameth-

ylammonium acetate (Scheme 14).^[49] The resulting *N*-cyanosulfilimines **62** are precursors for biologically relevant sulfoximines. The protocol utilizes 1.25 eq. tetramethylammonium acetate as a supporting electrolyte, while the acetate anion can serve as an oxidative electron transfer mediator. This publication also describes the possibility of a direct electron transfer from the thioether to the anode due to similar oxidation potentials of the anion and the sulfur substrate.

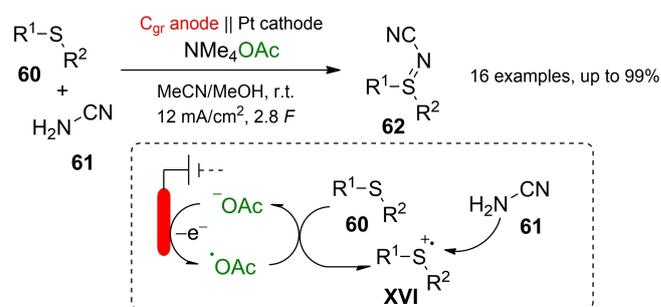
3.2. Category F (anion as hydrogen atom transfer mediator)

This category's examples discuss the hydrogen atom transfer ability of the supporting electrolyte anions as mediators. The anodic oxidation of an anion leads to a radical species that induces a hydrogen atom transfer (HAT), also known as proton-coupled electron transfer (PCET). This section presents two common literature-mentioned HAT-type mediators.

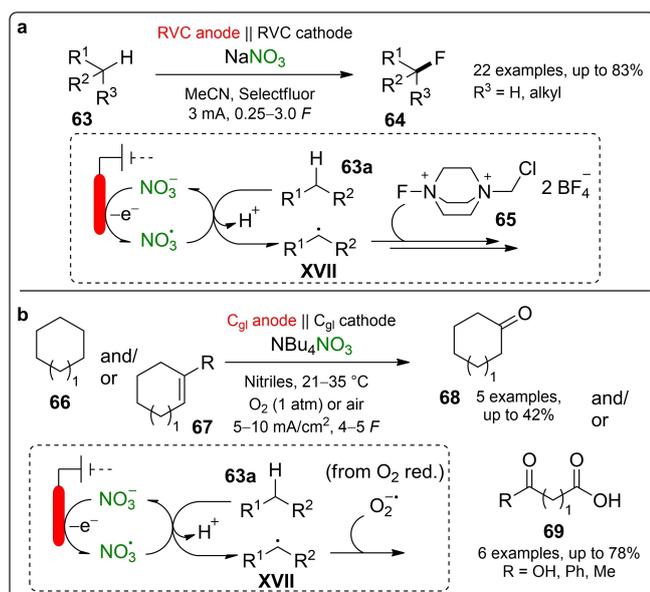
In 2019, the Baran group reported a protocol for electrochemical fluorination of C(sp³)-H bonds using sodium nitrate as a supporting electrolyte and anodic mediator (Scheme 15a).^[50] The reactions are conducted in acetonitrile at reticulated vitreous carbon (RVC) electrodes with an alternating polarity every two minutes. A wide variety of activated and non-activated C-H bonds could be functionalized using Selectfluor as a fluorinating agent, contributing partially to the ionic conductivity of the electrolyte.

Another nitrate-mediated protocol, tackling the oxo-functionalization of cycloalkanes and -alkenes, has been recently published (Scheme 15b).^[51] Tetrabutylammonium nitrate is presented in a dual role as a supporting electrolyte and a mediator in acetonitrile and isobutyronitrile solvents. Nitrate undergoes one-electron oxidation, while molecular oxygen is reduced to superoxide radicals at glassy carbon electrodes. Via an electron abstraction from the substrate, nitrate is regenerated. Parallel, the alkyl radical recombines with the cathodically reduced superoxide via convergent-type electrolysis, facilitating the effective transformation of cycloalkanes to the corresponding ketones **68**. Moreover, the same method could be extended to the double bond cleavage of alkenes to the corresponding carboxylic acids **69** as well.

The second frequently reported HAT mediator is iodide. Due to its low oxidation potential, the electrooxidation of iodide



Scheme 14. Acetate-mediated dehydrogenative oxidation of thioethers to *N*-cyanosulfilimines.^[49]

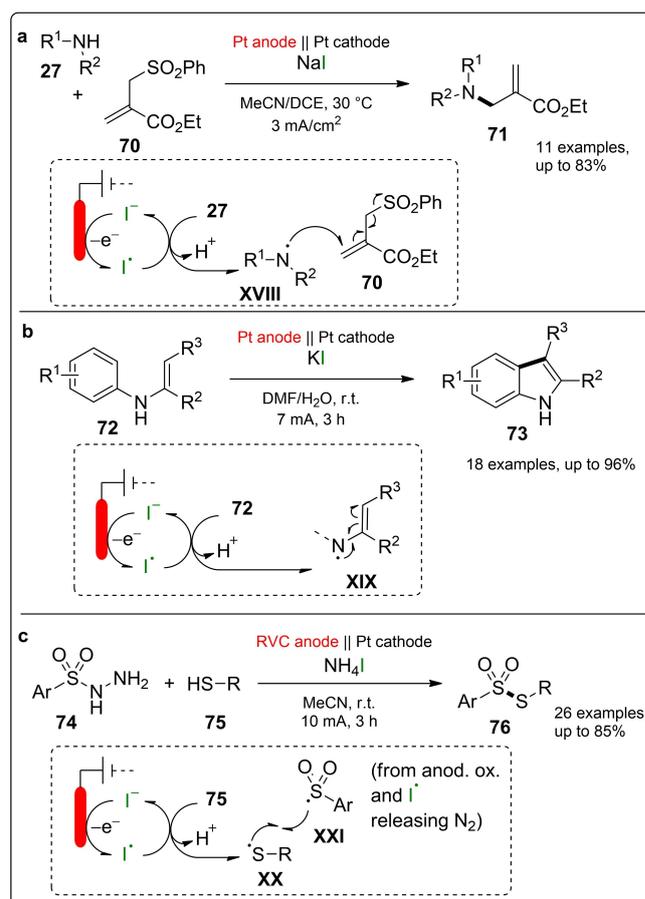


anions to iodine radicals is often described in the literature. Accordingly, it is a popular choice to encourage radical-induced cyclization and coupling reactions in a highly selective fashion. The groups of Zeng and Sun reported a sodium iodide-mediated synthesis of allylamines via a radical trapping sequence (Scheme 16a).^[52] The oxidatively generated iodine radical selectively abstracts a hydrogen atom of the sulfonamides or imides substrates as a first step. The resulting radical **XVIII** reacts with the allyl sulfone double bond **70**, releasing a sulfonyl radical and forming the allylamine product **71**, respectively. The reaction is performed in an undivided cell equipped with platinum electrodes.

The Lei group reported a similar example of nitrogen-centered radicals, performing an intramolecular oxidative annulation reaction to synthesize indoles from *N*-aryl enamines (Scheme 16b).^[53] 7.5 eq. potassium iodide serves as a supporting electrolyte and mediator in a DMF/water solvent mixture. Anodic generation of iodine radicals leads to an N-H bond dissociation, similar to the previous example. Here, the N-centered radicals perform an intramolecular cascade cyclization, resulting in the final products **73**. The corresponding imidazo[1,2-*a*]pyridines products could also be obtained by utilizing *N*-pyridyl enamines as substrates.

Chen et al. managed an electrochemical synthesis of iodide-mediated thiosulfonates from thiols and sulfonyl hydrazides (Scheme 16c).^[54] The protocol leads to an S-S coupling via an anodically generated iodine radical hydrogen abstraction from the thiol species. Simultaneously, the sulfonyl hydrazide **74** undergoes an anodic oxidation or oxidation with iodine radicals, releasing molecular nitrogen. Recombination of the two sulfur-centered radicals forms the final products **76**. The publication also reports promising results of the thiosulfonate

products for anticancer activities towards human tumor cell lines, investigated via a methylthiazolotetrazolium (MTT) assay.



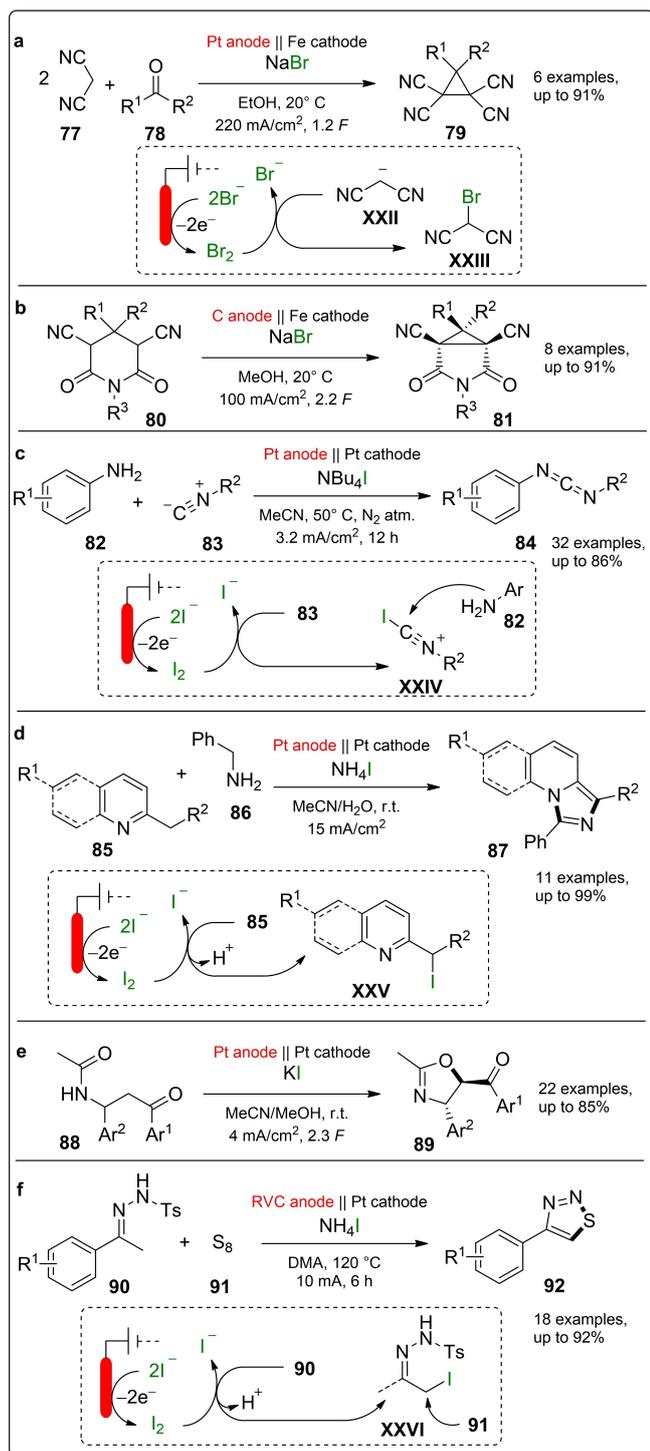
products for anticancer activities towards human tumor cell lines, investigated via a methylthiazolotetrazolium (MTT) assay.

products for anticancer activities towards human tumor cell lines, investigated via a methylthiazolotetrazolium (MTT) assay.

3.3. Category G (halide mediation)

Indeed, the most frequently used electroactive mediators that are serving simultaneously as supporting electrolytes are halide salts. Ammonium, alkylammonium, or alkali halide salts are very popular in organic electrochemistry. Bromide^[55] proved especially efficient, as the in-situ formed C-Br, N-Br, or S-Br bonds can be easily modified via nucleophilic substitution.

Nikishin et al. showed in the early 1990s an example of a cyclopropane formation reaction using sodium bromide as a supporting electrolyte and mediator (Scheme 17a).^[56] The electrochemically generated bromine reacts with a deprotonated malononitrile **XXII** to form an intermediate C-Br bond. Ethanolate serves as an in-situ generated base responsible for the malonate formation. Followed by a C-C bond formation with a second equivalent malononitrile, subsequent deprotonations, and a condensation reaction with a ketone, the desired cyclopropyl derivative **79** is formed. The method presents a



Scheme 17. Halide-mediated electrochemical cyclization for C–X bond formation. **a** Cyclopropane formation from malononitriles and ketones using NaBr.^[56] **b** Intramolecular cyclopropane formation using sodium bromide.^[57] **c** Carbodiimide synthesis from amines and isocyanides applying NBu_4I as a mediator.^[58] **d** Ammonium iodide mediated synthesis of 1,3-disubstituted imidazo[1,5-a]quinolines.^[59] **e** Cyclization of β -amino arylketones to trisubstituted 2-oxazolines using potassium iodide.^[60] **f** Synthesis of 1,2,3-thiadiazoles from *N*-tosyl hydrazones and elemental sulfur using ammonium iodide.^[61]

limited scope but high yields. Years later, a similar procedure for a cyclopropane formation for an intramolecular cyclization reaction was also reported (Scheme 17b).^[57]

Sharma et al. reported the iodide-mediated electrochemical cross-coupling of amines and isocyanides to synthesize carbodiimides (Scheme 17c).^[58] The reaction was performed in an undivided cell at platinum electrodes with hydrogen formation as the counter-reaction. Further functionalization was illustrated by converting the carbodiimides in-situ into unsymmetrical ureas, using an electricity ON-OFF strategy.

An electrochemical synthesis of 1,3-disubstituted imidazo[1,5-a]quinolines **87** has been shown by Wang et al. applying 1.0 eq. ammonium iodide as a supporting electrolyte (Scheme 17d).^[59] In-situ C–I bond formation leads to an activation of the quinoline substrates for a subsequent substitution reaction, followed by additional oxidation steps and an amination to form the corresponding products.

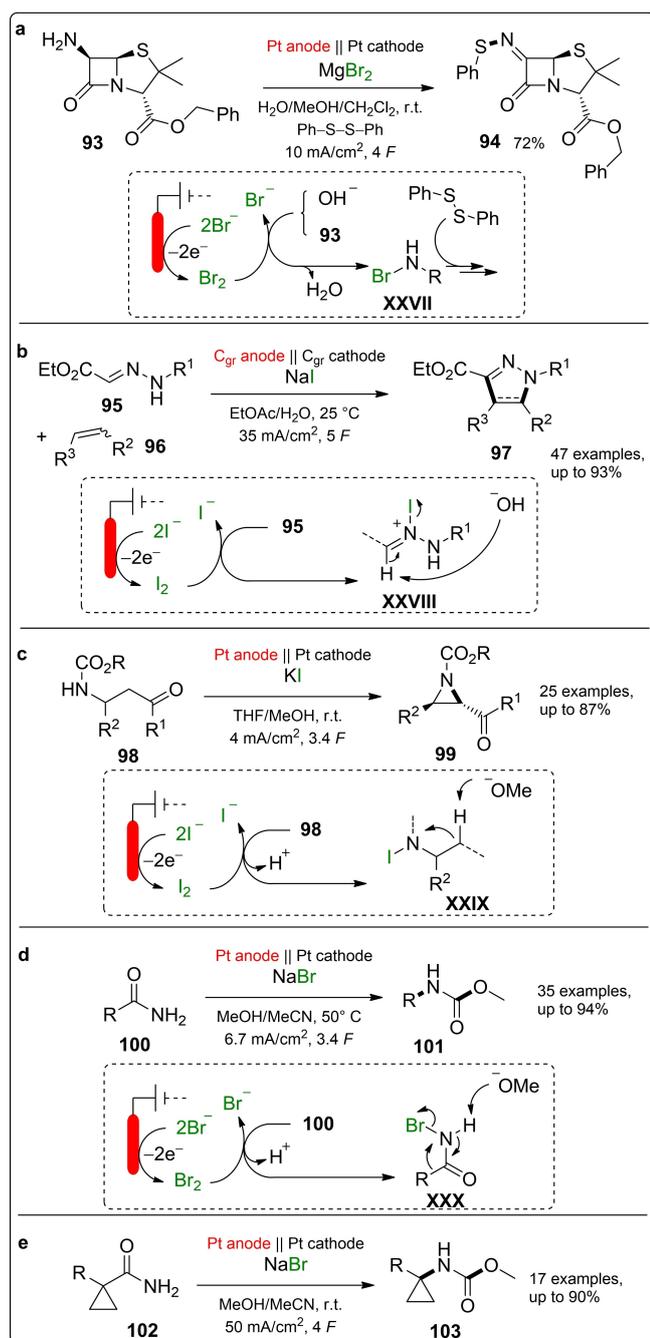
Another cyclization protocol describes the dehydrogenative cyclization of β -amino arylketones to trisubstituted 2-oxazolines (Scheme 17e).^[60] Potassium iodide is used for iodination of the C–H acidic α -position of the ketone group. A nucleophilic substitution of the amide's oxygen leads to cyclization and the respective oxazoline product formation.

Using elemental sulfur, the method from Tang et al. represents an exclusive metal- and oxidant-free electrochemical protocol for synthesizing 1,2,3-thiadiazoles (Scheme 17f).^[61] Here, 20 mol% ammonium iodide is employed as a mediator, providing the iodination of a C–H acidic α -position next to the substrate's *N*-tosyl hydrazone group. Upon iodination, the sulfur is implemented in that position, paving the way for the *S,N*-heterocycle formation.

Torii et al. described a procedure for the electrochemical N–X bond formation, representing the bromide-mediated transformations of α -aminoalkanoates and diaryl or dialkyl disulfides to sulfenimines (Scheme 18a).^[62] Magnesium bromide is applied as a supporting electrolyte and electroactive mediator, describing the selective bromination of the substrate's amino moiety. The same conditions could also be applied to the late-stage sulfonylation of biologically active penicillin and cephalosporin.

An iodine-mediated synthesis of pyrazolines and pyrazoles using a [3 + 2]-dipolar cycloaddition was presented in our research group (Scheme 18b).^[63] These essential structural motifs for pharmaceutical agents were formed from hydrazones **95** and dipolarophiles **96**. A biphasic ethyl acetate and water system was applied using sodium iodide as a supporting electrolyte. N–I bond formation of the hydrazone's nitrogen activates the substrate for a 1,3-dipole formation. The commercial herbicide safener mefenpyr-diethyl synthesis was presented as a highlight for this elegant and scalable protocol, allowing hectogram quantities.^[64]

A different iodide-mediated protocol was reported for the electrochemical synthesis of aziridines via the N–H bond activation (Scheme 18c).^[65] With potassium iodide as a mediator role, external oxidants are avoided, and the reaction is complimented by the cathodic evolution of hydrogen as the byproduct. The activated N–I bond promotes an intramolecular



Scheme 18. Electrochemical halide-mediated N–X bond formation. **a** Sulfenimine synthesis from penicillin, using 1,2-diphenyldisulfane and magnesium bromide as a mediator.^[62] **b** [3 + 2]-Dipolar cycloaddition for synthesizing pyrazolines and pyrazoles using sodium iodide.^[63] **c** Iodine-mediated intramolecular cyclization to *trans*-2,3-disubstituted aziridines.^[65] **d** Electrochemical Hofmann rearrangement of several amides to carbamates using sodium bromide.^[67] **e** Electrochemical Hofmann rearrangement of cyclopropylamides.^[68]

cyclization to generate *trans*-2,3-disubstituted aziridines **99** in good yields.

The electrochemically induced Hofmann rearrangement has received significant attention in the recent years. Pioneering work was presented by Matsumura and Satoh using NaBr in a methanol/acetonitrile mixture solution.^[66] Based on these

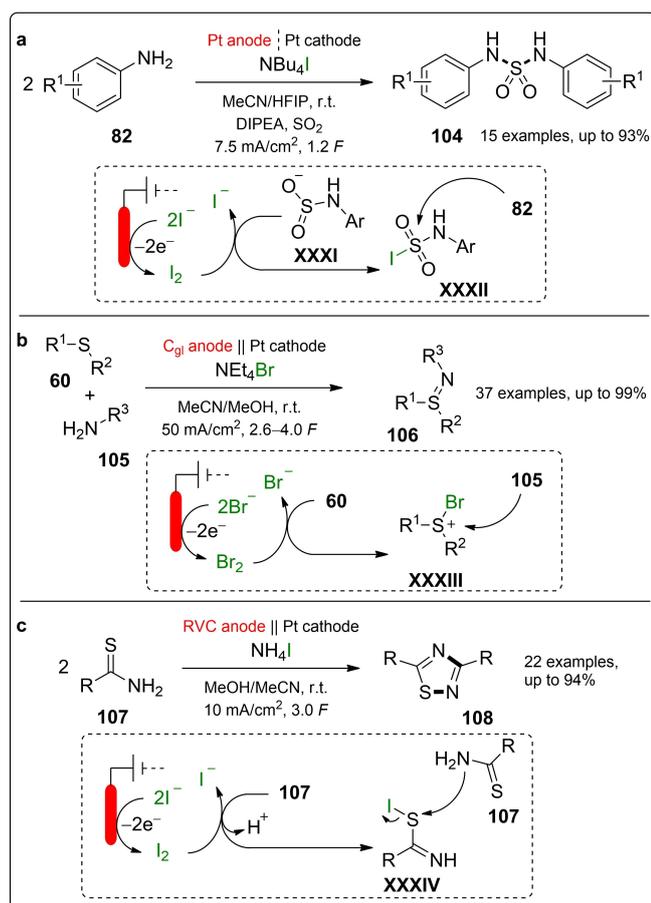
results, modern protocols increasingly contribute to the scope of their applications. In 2018, Xu, Zhang, and co-workers published a broadly applicable electrochemical protocol to synthesize bioactive carbamates from amides (Scheme 18d).^[67] Sodium bromide is employed as an inexpensive bench-stable salt, generating bromine in-situ at the anode. The reaction is complemented by the cathodic generation of methanolate, supporting the rearrangement. 50 mol% NaBr was sufficient to omit any additional supporting electrolytes and provide 31 carbamate products **101** with up to 94% yields. Moreover, biologically active, steroid, or adamantane-like carbamates could also be obtained.

Similarly, the electrochemical bromide-mediated rearrangement of cyclopropylamides to the corresponding carbamates was also published, exploiting the selective conversion of these delicate substrates (Scheme 18e).^[68] Similar to the previous approach, this protocol uses the NaBr/MeOH redox system to form 17 examples with up to a 90% yield. The same concept was recently applied for the electrochemical modification of acrylamide-containing copolymer scaffolds for the first time. The primary amide chains serve as “masked” isocyanates to form the alkyl/aryl-*N*-vinyl carbamate copolymers. While this method’s limitations and scope are still under investigation, it demonstrates the potential industrial suitability of the electrochemical Hofmann rearrangement.^[69] Multigram-scale applicability was demonstrated by C. Kappe and D. Cantillo using a spinning electrode chemical reactor. With a unique graphite felt anode and cell design, the e-Chem induced Hofmann-rearrangement of 2-phenylacetamide was realized on a 400 mmol scale using flow recirculation mode. The corresponding carbamate was obtained with 95% yield and 97% purity.^[70]

Substitution reactions were also shown on sulfur atoms upon S–X bond formation. The generation of symmetric sulfamides from anilines and an SO₂ stock solution was recently published (Scheme 19a).^[71] Tetrabutylammonium iodide (0.10 eq.) was employed in a dual role as a mediator and electrolyte. The sulfuramidite intermediate is activated via an in-situ S–I bond formation, making it vulnerable to a nucleophilic attack from another aniline to yield the final product **104**.

Another method for halogenating low-valent sulfur compounds was reported with the dehydrogenative imination with primary amides. (Scheme 19b).^[72] The protocol provides an electrochemical pathway for synthesizing sulfilimines, sulfoximines, sulfinamidines, and sulfinimidate esters employing tetraethylammonium bromide.

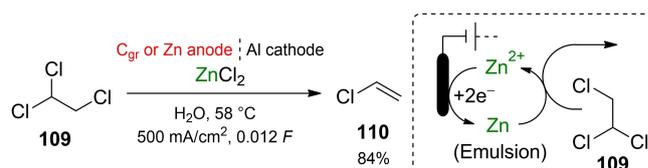
A method for the formation of 3,5-disubstituted-1,2,4-thiadiazoles via dimerization of thioamides has been reported using ammonium iodide in a dual role (Scheme 19c).^[73] After the iodination of the substrate’s sulfur atom, the intermediate **XXXIV** further reacts with another thioamide molecule. Instantly, an intramolecular condensation occurs, liberating the desired molecule **108** and hydrogen sulfide by-product



Scheme 19. Electrochemical halide-mediated S–X bond formation. **a** Generation of symmetric sulfamides from anilines and a SO_2 stock solution using NBu_4I .^[71] **b** Dehydrogenative imination of sulfur compounds with primary amides with NEt_4Br .^[72] **c** Dimerization of thioamides to 3,5-disubstituted-1,2,4-thiadiazoles using ammonium iodide.^[73]

3.4. Category H (cation as reductive electron transfer mediator)

As a cathodic equivalent to category E, this category was conceived to exhibit examples of using dual-role cations as reductive electron transfer mediators. Notably, only one protocol could fit this classification, describing the envisioned characteristics for category H. In 1981, Pletcher et al. described a procedure to cathodically generate zinc powder from zinc chloride, applying high current densities. In the presence of elemental zinc, nitrobenzenes were indirectly reduced to the corresponding anilines. Moreover, using the same methodology, the dechlorination 1,2,2'-trichloroethane was also described (Scheme 20).^[74] The reaction was performed at a current density range of 50–500 mA/cm^2 in a biphasic system of water and organic substrate. In this emulsion, the in-situ generated zinc powder provides a high metal surface area, a passivation-free layer on the surface, enhancing its reactivity.



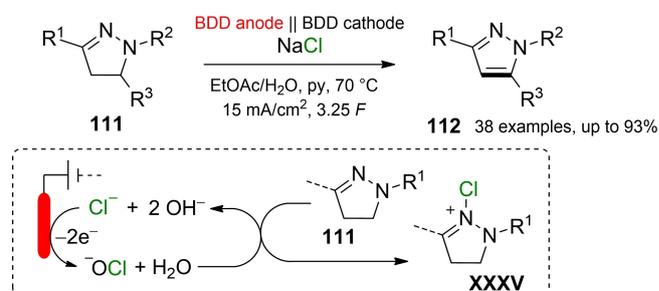
Scheme 20. Electrochemical generation of zinc powder from zinc chloride supporting electrolyte to foster the reduction of organic compounds.^[74]

4. Miscellaneous

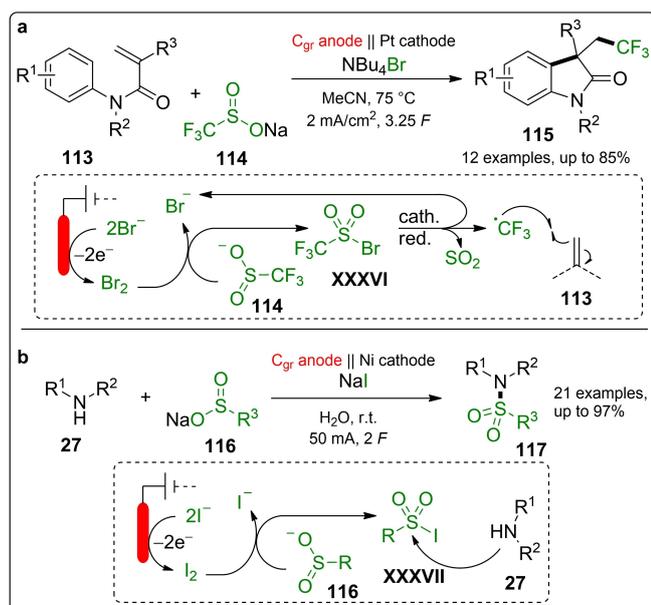
Although most dual-role protocols exhibit a clear mechanistic pathway, some examples could not be confidently classified. This section covers reported protocols in which mechanistic aspects did not match the preset criteria, but a dual role of the supporting electrolytes is evident. Fuchigami et al. reported the anodic allylation of *S*-functionalized thiophenols, where both the substrate and the allylation reagent contain the tetrabutylammonium alkyltrifluoroborate moieties, contributing to conductivity, and simultaneously taking on their roles as substrate and reagent in the reaction.^[75]

Waldvogel and co-workers developed a procedure for the aromatization of pyrazolines to pyrazoles using sodium chloride as a supporting electrolyte (Scheme 21).^[76] Even though the chloride anions are the electroactive species and, therefore, serving in a dual role, the in-situ formation of hypochlorite by reaction with cathodically generated hydroxide is a critical mechanistic point. Hypochlorite is the species that induces aromatization by forming the reactive N–Cl bond of **XXXV**. The reaction is performed in a biphasic system in an undivided cell at carbon-based electrodes. Technical scalability is provided by the simple extraction and distillation work-up procedures.

The following protocols in Scheme 22 can be described as a combination of categories A and G. Both employ sodium sulfonates and halide salts contributing to the electrolyte's ionic conductivity, with the halide being the electroactive species. The protocol from Zeng and co-workers shows a combined trifluoromethylation and cyclization of *N*-arylacrylamides **113**, in the presence of tetrabutylammonium bromide and sodium trifluoromethanesulfonate (Scheme 22a).^[77] After anodic oxidation of bromide to bromine, trifluoromethanesulfonyl bromide (**XXXVI**) is formed, liberating SO_2 and a trifluoromethyl radical



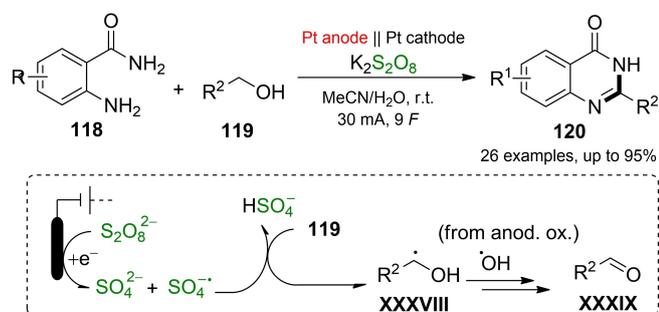
Scheme 21. Electrochemical aromatization by applying sodium chloride in a dual role, whereby hypochlorite is formed as aromatization inducing reagent.^[76]



Scheme 22. Combinations of categories A and G. **a** Trifluoromethylation/cyclization using bromide and trifluoromethanesulfonate salts.^[77] **b** Iodine-mediated sulfonamide synthesis from sulfonate salts.^[78]

upon cathodic reduction. Addition to the substrate's double bond starts the radical cascade for the cyclization that results in the formation of **115**.

Comparably, a protocol from Yuan and co-workers describes the formation of sulfonamides by *N*-sulfonation with sulfonate salts (Scheme 22b).^[78] Iodide anions are used here as the electroactive species forming in-situ arylsulfonyl iodide **XXXVII**, suffering a nucleophilic attack by the amine substrate. The protocol features water as a green solvent for sulfonamide synthesis at graphite anode. An unusual approach for a cathodically induced HAT is presented by Ke and co-workers (Scheme 23).^[79] Peroxydisulfate anions are reduced to sulfate and sulfate radicals. The latter serves as the HAT reagent, activating the alcohol substrates in the alpha position, furthering its oxidative conversion to an aldehyde **XXXIX**. After condensation to the 2-aminobenzamide derivative, oxidation to the final quinazolinone product **120** occurs. The reaction is performed as a one-pot procedure in an undivided cell with



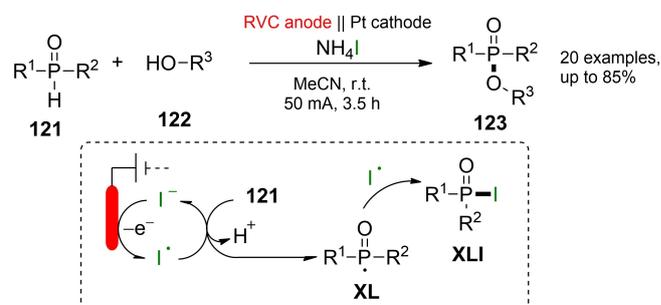
Scheme 23. Cathodically induced HAT by using peroxydisulfate anions as electroactive species for a formation of quinazolinones.^[79]

constant current conditions and exhibits a high tolerance towards functional groups.

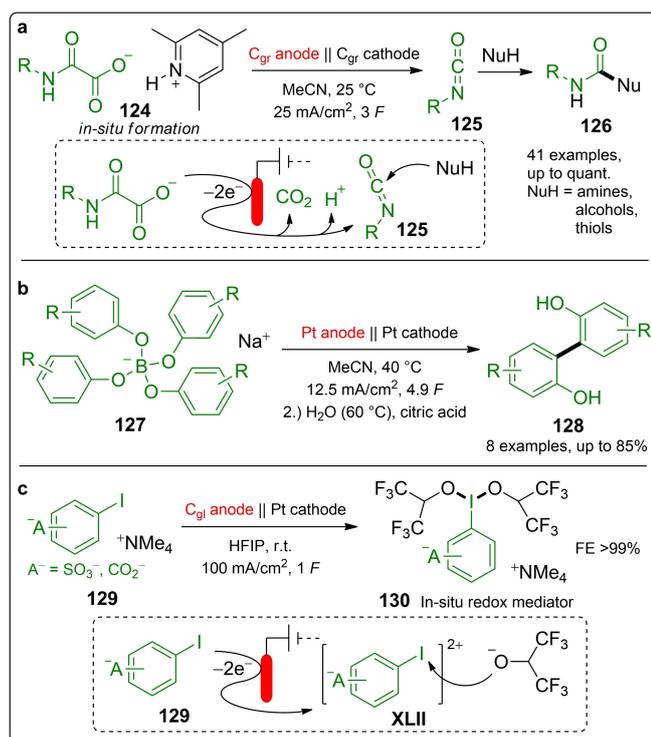
A combination of categories F and G can best describe the following procedure published by Tang and co-workers. The oxidation of secondary phosphine oxide substrates into phosphinate products is described using 15 mol% ammonium iodide as an electroactive HAT mediator, generating phosphine oxide radicals that recombine with iodine radicals (Scheme 24).^[80] The mechanistic explanation were demonstrated with control and cyclic voltammetry experiments.

Another unusual case that could not be included in the categories describes the dual role of a substrate as the supporting electrolyte itself. Two example protocols are presented in Scheme 25 to depict the idea mentioned above. The Lam group published a fully-fledged method, providing access to a broad range of amide groups containing products like ureas, carbamates, and thiocarbamates, starting from oxamic acids (Scheme 25a).^[81] Elegantly, the substrate accommodates an *N*-alkyloxamic acid collidinium salt, simultaneously serving as a supporting electrolyte. Subsequent to decarboxylative oxidation, an isocyanate intermediate **125** is formed, which reacts further in a second step with protic nucleophiles like amines, alcohols, and thiols to the corresponding products. Furthermore, a single-pass electrochemical flow reaction facilitated the formation of certain urea compounds that could not form in batch-type cells.

A different protocol uses sodium tetraphenoxyborate derivatives as substrates and supporting electrolytes (Scheme 25b).^[82] Within this template-directed approach, substituted phenols were electrochemically homo-coupled to the corresponding 2,2'-biphenols **128** by oxidizing the anion of the electrolyte. Especially methyl-substituted phenols showed promising results. Due to the spatial proximity, selective *ortho*-coupling could be achieved. Francke et al. thoroughly investigated the preparation of dual role hypervalent iodine derivatives in a mediator role, from iodoarenes **129** including the carbonate or sulfonate moieties in *ortho*, *meta*, or *para* positions to the iodo-group. HFIP solvent promoted the iodo-group's selective activation over the anionic functionalities, allowing the mediated synthesis of carbazoles, aromatic substitution of different anilides, and the cyclization of *N*-allylamides in an ex-cell approach (Scheme 25c).^[83]

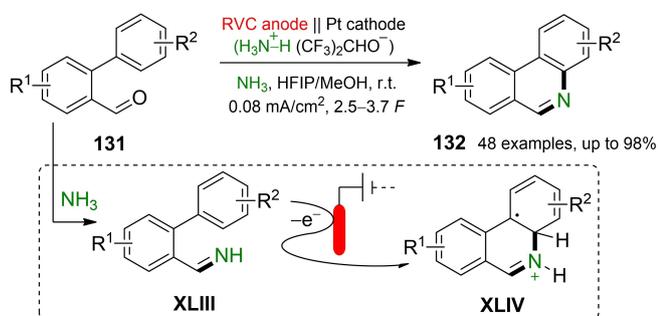


Scheme 24. Oxidation of secondary phosphine oxides to phosphinates by a combination of categories F and G approach, using ammonium iodide.^[80]



Scheme 25. Example protocols describing the dual role of compounds as substrates and supporting electrolytes. **a** Anodic decarboxylation of oxamic acids to isocyanates for nucleophilic additions.^[81] **b** The substrates tetraphenylborate anions serves as templates for *ortho*-selective coupling to 2,2'-biphenols.^[82] **c** In-situ formation of hypervalent iodoarene species as redox mediators for different dehydrogenative coupling reactions, FE: Faradaic efficiency.^[83]

An example shown by Xu and co-workers is conducted in the absence of a bench-stable supporting electrolyte (Scheme 26).^[84] Instead, ionic conductivity occurs from an acid-base proton-transfer reaction of ammonia and HFIP. Ammonium, therefore, serves as the electrolyte cation. At the same time, ammonia reacts with the aldehyde substrate **131**, leading to the in-situ formation of **XLIII** that promotes an intramolecular C–N coupling after the anodic oxidation. The method was demonstrated with a broad scope of products,



Scheme 26. In-situ ammonium used in a dual role as reactant and supporting electrolyte to form *N*-heterocyclic compounds from biaryl aldehydes.^[84]

casting phenanthridines and other structurally related polycyclic *N*-heteroaromatic compounds with yields up to 98%.

5. Summary and Outlook

Electrochemical approaches can be engineered in a cost-effective and material-conscious way to display sometimes unexpected reactivity.

The definition of supporting electrolytes as sole conductivity-providing agents has been transformed into a more flexible analogy. The rigid metaphor of a disposable entity evolved into a dual-role agent that exhibits both the characteristics of a supporting electrolyte and a reagent, simplifying electrochemical procedures in terms of cumbersome work-up procedures and generating unnecessary waste products. Nevertheless, we cannot ignore certain limitations in terms of the obligatory excessive amounts of salts or the choice of solvent to provide a stable and selective electrochemical window. The reflection of the “good, but not enough” concept forced this generation's synthetic chemist to think outside the box and use supporting electrolytes in a mediator role. This perspective sets both roles in equally important positions, focusing more on the recovery and recycling of these agents, providing a more sustainable and resource-saving approach for electrochemical synthesis.

We summarized promising electrochemical synthesis protocols where the supporting electrolyte is utilized in a dual role, either as a reagent or a mediator. The subcategories were defined with regards to the proposed mechanistic aspects of the respective literature reports. We found that dual-role supporting electrolytes are most frequently used in methodologies where substrate oxidation occurs first (category A) or is mediated by different halide anions (category G) to achieve the reactivity of interest. While other categories where the cation reduction is the principal step (categories D and H) or where the anions serve as oxidative electron transfer agents only cast a handful of examples. The mechanistic definition of these categories implies challenging reaction development, which is not commonly reported.

The authors do not claim the integrality of the literature-known examples that were classified and categorized in the review. Instead, we invite other research groups to contribute and complement the categorizations or to add more protocols, especially to categories lacking examples. This paper is a source of inspiration to drive electrochemical reaction design in a more resource-saving direction.

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Conflict of Interests

The authors declare no conflict of interest.

Keywords: Electrochemistry · Organic synthesis · Radical reactions · Redox chemistry · Supporting electrolyte

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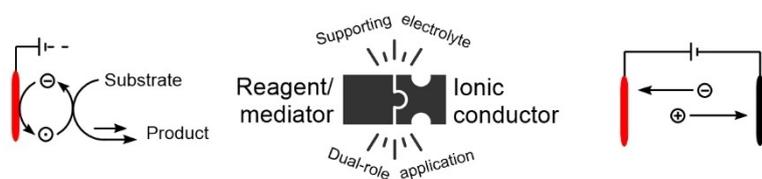
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REVIEW



“The perfect combination does not exist... Wait a sec!” This review concludes promising organic electro-synthesis protocols with examples that comprise supporting electrolytes used in a dual role as ionic conductors and reagents or electroactive mediators. Several categories have

been defined, systematically sorting the presented dual-role applications. This review about the electrolyte constituent's dual role is meant to inspire organic electrochemists to pursue reaction development in a material-saving fashion.

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Dual Roles of Supporting Electrolytes in Organic Electrosynthesis