

Use of Sacrificial Anodes in Synthetic Electrochemistry. Processes Involving Carbon Dioxide*

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Electrochemical syntheses involving carbon dioxide by the use of sacrificial anodes in diaphragmless cells are widely applied on a laboratory scale, and in some cases have been scaled up to the pilot plant stage or to industrial production. In several cases noteworthy improvements have been observed in yields and selectivities with respect to the results obtained with conventional diaphragm electrolytic systems. In this review both processes involving carbon dioxide alone and electrocarboxylations of various classes of organic compound are taken into consideration.

A broad definition of sacrificial electrodes, as far as anodic processes are considered, extends to all those metal electrodes for which, upon anodic polarization, the oxidation of the metal itself [reaction(1)] is favoured, for thermodynamic and/or kinetic reasons, with respect to all the other reactions involving the species present in the neighbourhood of the electrode.



Sacrificial anodes in synthetic electrochemistry appeared in the early twenties, when lead or bismuth alkyls were obtained by electrolysis of ethylsodium dissolved in diethylzinc and triethylaluminium with lead or bismuth anodes.^{1,2} This pioneering work was followed, in the fifties, by a thorough study by Ziegler and Lehmkuhl³ on the electrolytic behaviour of complex organoaluminium compounds. In this context the anodic dissolution of aluminium in the presence of organic halides and/or of various organometallic species was investigated, both for the deposition of the metal on various cathodes, and for the synthesis of metal alkyls.

Since then several syntheses of organometallics have been performed electrochemically via the corresponding sacrificial electrode,^{4,5} and among them that of tetraethyllead was developed up to industrial production.⁶

Sacrificial anodes have been also proposed, essentially on a laboratory scale, for the performance of quite a large number of electrochemical syntheses in non-aqueous media. In this last case the redeposition of the metal at the cathode is generally undesired, the cathodic reaction being

useful to the synthetic process. In this connection it should be considered that the redox potential of reaction (1) is generally shifted towards more negative values by the formation of complex compounds between M^{n+} ions introduced into the electrolytic medium by the anodic reaction and anionic species originating at the cathode, which in several cases are very good chelating agents.

It appears immediately evident that, with a proper choice of the metal as the anode, it is possible to use undivided cells for the performance of cathodic processes leading to easily oxidizable products, instead of using diaphragms or membranes. This methodology has resulted, particularly advantageously, in the arrangement of high-pressure small-scale electrochemical reactors.⁷ Interesting results have also been obtained in the syntheses of various complexes of transition metals,^{8–15} via combined anodic and cathodic reactions.

A new and interesting coupling of anodic dissolution of various metals (Mg, Al, Zn) to cathodic reactions involving organic halides catalysed by nickel complexes has been proposed recently for the performance of numerous electrosyntheses.¹⁶

In this paper processes involving carbon dioxide by means of electrochemical systems using sacrificial anodes are reviewed.

The reduction of carbon dioxide alone

The first communication on the electrochemical reduction of carbon dioxide to oxalate in aprotic media with Al sacrificial electrodes, in the diaphragmless system summarized in Scheme 1, was published in the early seventies.¹⁷

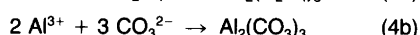
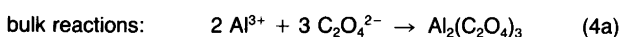
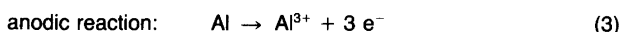
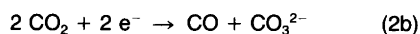
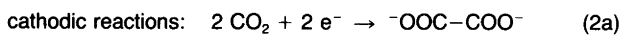
Aluminium oxalate (current yields up to 38%), and CO and carbonate (current yield 47%) were obtained as primary products of the synthesis. In the same period several

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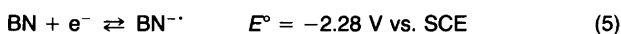
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(anode) Al/SSE, CO₂ (*p* = 1.4–31 atm)/M (cathode)where SSE = N,N-dimethylformamide + Bu₄NBr 0.1 M

M = stainless steel AISI 316, mercury

*Scheme 1.*

other laboratories published the same synthesis in conventional diaphragm cells.^{18,19} The reduction of carbon dioxide takes place at potentials far more negative than the related E° , estimated as -2.21 V vs. SCE .²⁰ In fact, carbon dioxide presents a reduction peak, irreversible at ordinary scan rates, the cathodic potential of which (around -2.8 to -2.9 V vs. SCE)²¹ depends on the nature of the electrode and on the composition of the reaction medium. A synthetic way of performing this reduction at a cathodic potential less negative than in uncatalysed systems has been proposed,²² based on the use of benzonitrile ($E^\circ = -2.28 \text{ V SCE}$), acting as a homogeneous charge-transfer agent (Scheme 2). In this way the reduction of carbon dioxide,



BN = benzonitrile

Scheme 2.

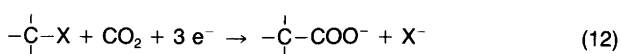
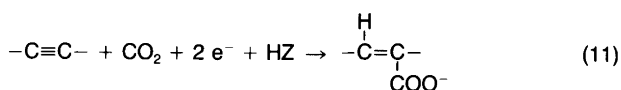
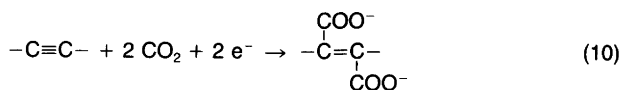
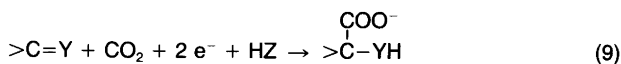
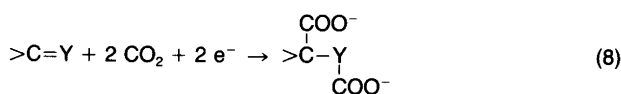
coupled to the anodic dissolution of aluminium, takes place at the reduction potential of benzonitrile. The synthesis with benzonitrile gave current yields around 70%; the reduction process does not appear to be influenced by the Al(III) species fed into the reaction medium by the anodic reaction.

An electrochemical synthesis of oxalic acid by reduction of carbon dioxide in aprotic media with zinc sacrificial anodes was brought to pilot scale by the DECHEMA Institute some years ago.²³ The synthesis is performed with zinc anodes; after the hydrolysis of zinc oxalate, the mother liquors are sent to a recovery unit of the metal, from which zinc can be recycled to the electrosynthesis unit. Current and product yields respectively of 85% and 90% are claimed. This system, which, in principle, does not pose problems of waste disposal, could become competitive with the existing chemical methods should the latter incur higher costs as a result of more severe environmental restrictions.

Electrocarboxylations

A precise influence of the sacrificial anode (or better of the cations sent into the reaction medium by the anodic reaction) on product or faradaic yields was not observed in all the examples quoted in this chapter. However, mono- or poly-carboxylated anions always gave rise to complex salts with the metal cations, which are insoluble in the reaction medium, or can be made insoluble by addition of appropriate co-solvents, making the isolation procedures easy and straightforward.

The stoichiometries of various electrocarboxylation reactions are presented in Scheme 3. For substrates (R) more easily reducible than carbon dioxide two possible pathways have been considered for the reaction mechanism, after the production at the electrode of the anion radical $\text{R}^{\cdot-}$: (i) a nucleophilic attack of $\text{R}^{\cdot-}$ on carbon dioxide, followed by further reduction of the resulting carboxylated anion radical $\text{RCO}_2^{\cdot-}$ at the potential of formation²⁴ and (ii) a homogeneous charge-transfer reaction of $\text{R}^{\cdot-}$ with CO_2 followed by coupling of the anion radicals $\text{R}^{\cdot-}$ and $\text{CO}_2^{\cdot-}$.^{25,26} Since, according to the Marcus theory, the rate of the outer-sphere charge transfer between $\text{R}^{\cdot-}$ and CO_2 is expected to increase with the standard Gibbs energy of the reaction, the standard potential difference $\Delta E^\circ = E^\circ(\text{CO}_2/\text{CO}_2^{\cdot-}) - E^\circ(\text{R}/\text{R}^{\cdot-})$ is expected to provide useful information on the competition. It has been deduced, on the grounds of kinetic evidence, that when ΔE° is lower than about -400 mV , the mechanism involving nucleophilic attack as the initial step should be predominant.²⁶ In contrast, for substrates reducible in a very negative potential range ($\Delta E > -400 \text{ mV}$), the homogeneous charge-transfer mechanism becomes predominant, with rather complex follow-up reactions.^{20,27} The examples quoted hereafter are representative of the wide variety of synthetic possibilities opened up by the combination of cathodic carboxylation and anodic dissolution of a metal.



Where Y = C<; N-; O; HZ = proton donor;
X = Cl, Br, I, -SR, -O-CO-R.

Scheme 3.

Electrocarboxylation of olefins. In the case of acenaphthylene ($E^\circ = -1.70$ V vs. SCE), for which $\Delta E^\circ < -400$ mV, no charge-transfer processes are involved in the reaction mechanism. This electrocarboxylation was investigated in our laboratory making use of sacrificial aluminium anodes.²⁸ Under anhydrous conditions *trans*-1,2-dicarboxy-acenaphthene is obtained as the aluminium salt insoluble in the reaction medium, with yields of up to 81%.

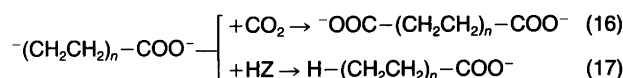
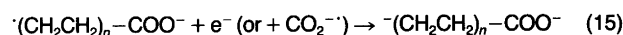
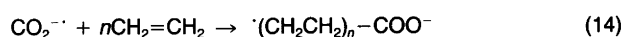
When proton donors and carbon dioxide are both present in the reaction medium, the formation of the dicarboxylic acid is almost completely suppressed, and the monocarboxylation derivative and acenaphthene are obtained with overall product yields from 85 to 95%. These data are in agreement with those reported by Savéant for the carboxylation of some activated olefins, such as some esters of cinnamic acid, in media of low proton availability.²⁶

Styrene^{20,27} shows an E° (-2.58 V vs. SCE) more negative than that of the couple $\text{CO}_2/\text{CO}_2^{\cdot-}$ but more positive than the actual irreversible reduction potential of carbon dioxide in aprotic media (-2.8 V vs. SCE in DMF). Therefore it is in the range of $\Delta E^\circ > -400$ mV, but under conditions suitable for styrene being itself the cathodic depolarizer. The cyclovoltammetric behaviour is consistent with the second reaction pathway summarized in the introduction to this section. The dicarboxylation, under strictly anhydrous conditions, takes place with yields of around 85%. The influence of proton donors on the reaction has been also explored: the carboxylation takes place invariably in the β -position and with yields of up to 69%, but with concomitant formation of ethylbenzene in much lower yields than in the previous cases of acenaphthylene and cinnamate esters. It is also possible to perform this electrocarboxylation making use of benzonitrile, which has already been described as being able to act as a homogeneous charge-transfer agent for the reduction of carbon dioxide alone. In this last case neither styrene nor carbon dioxide acts as cathodic depolarizer, only benzonitrile.

A third case, in which the olefin is reduced at more negative potentials than carbon dioxide, is represented by the electrocarboxylation of ethylene.¹⁷ From the cyclovoltammetric behaviour of the two starting materials it is confirmed that ethylene is involved in the reaction only in a chemical way. In this case, by electrochemical reduction of ethylene and carbon dioxide mixtures, dissolved under pressure in DMF/TBABr, with Al sacrificial anodes, a mixture of dicarboxylates and monocarboxylates of respective general formula $^-\text{OOC}(\text{C}_2\text{H}_4)_n\text{COO}^-$, and $\text{H}(\text{C}_2\text{H}_4)_n\text{COO}^-$ both with $n = 0, 1, 2, 3, 4$, as aluminium salts, is obtained.

The ratio of the product yields of each term (n) with respect to the $(n+1)$ is constant, on a semilogarithmic scale (Fig. 1), for the two series of di- and mono-carboxylic acids, suggesting a reaction mechanism, as far as initiation and propagation are considered, consisting of the sequence of radical reactions depicted in Scheme 4.

In the formation of the two series of carboxylic acids with



Scheme 4.

$n \geq 1$, surface processes take place most probably involving both carbon dioxide and ethylene, as demonstrated by the different slopes of the curves reported in Fig. 1 referring to the behaviour of systems having different cathodic materials.²⁹

Electrocarboxylation of alkynes and allenes. The reductive addition of carbon dioxide to substituted acetylenes in conventional diaphragm systems shows poor selectivity, leading to mixtures of fumaric, maleic and succinic acids in overall yields not exceeding 40%.³⁰ Better yields and unexpected regioselectivities are claimed by Duřach and Périchon, making use of catalytic systems having, as precursors, complexes of Ni(II) with various nitrogen-containing polydentate ligands. In all cases, synergy involving Mg(II) species arising from a sacrificial magnesium anode has been observed. Among the complexes proposed up to now $[\text{Ni}(\text{bipy})_3]^{2+}$,^{31,32} $[\text{Ni}(\text{PMDTA})]^{2+}$,^{33,34} and $[\text{Ni}(\text{TMEDA})]^{2+}$ ³⁴ (where *bipy* = 2,2'-bipyridine; PMDTA = *N,N,N',N''N''*-pentamethyldiethylenetriamine; TMEDA = tetramethylethylenediamine) have given better results. In general, substituted acrylic acids are obtained by electrocarboxylation of mono- or di-substituted acetylenes, and, with few exceptions, from α,ω -diynes. In particular

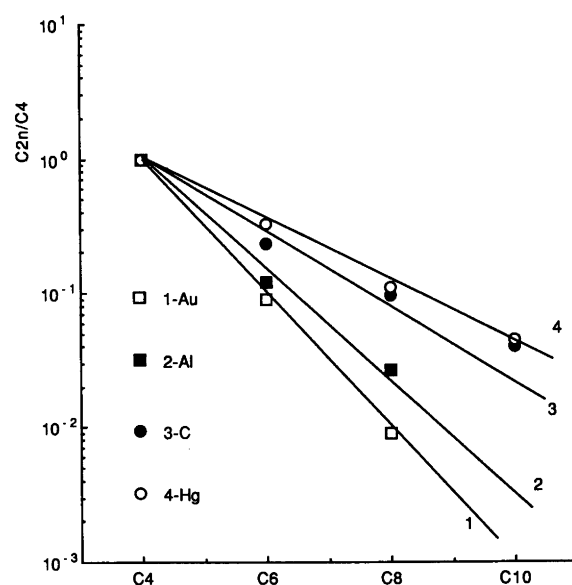


Fig. 1. Influence of the cathodic material on the carboxylation of ethylene.

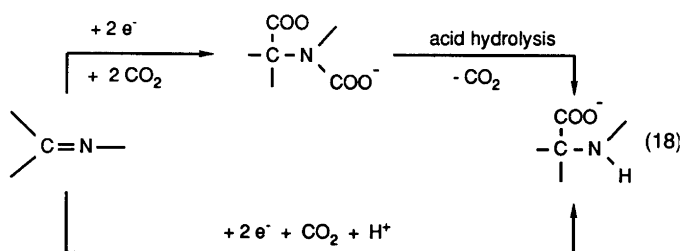
α -substituted acrylic acids, having the β -isomers as minor products, are obtained from quite a large variety of terminal alkynes ($R-C\equiv C-H$, where $R = \text{alkyl, benzyl, aryl}$) using, as catalyst precursors, the Ni complexes already quoted. Better results are obtained with $[\text{NiTMEDA}]^{2+}$, reaching, in the case of 1-octyne, overall yields of carboxylated products of up to 80%, with excellent selectivity towards α -carboxylation. In the case of α,ω -diynes³⁴ the carboxylation, with $[\text{NiPMDTA}]^{2+}$ and $[\text{NiTMEDA}]^{2+}$ invariably involves only one of the triple bonds, once again leading, with yields of up to 65% to α -carboxylation. In contrast $[\text{Nibipy}]_3^{2+}$ catalyses the cyclization and monocarboxylation of the diyne.

The same catalyst precursors have been also proposed for the carboxylation of allenes.³⁵ Better results, although with moderate selectivities, are reported with $[\text{NiPMDTA}]^{2+}$. The regioselectivity of the reaction is influenced by the structure of the starting molecules: acrylic acids are obtained from 1-alkyl and 1,1-dialkyl substituted allenes, whereas 1,3-dialkyl substituted allenes afford preferentially vinylacetic acids.

The electrocarboxylation of aldehydes and ketones. The electrocarboxylation of ketones to the corresponding α -hydroxy acids was first described by Wawzonek,³⁶ who reported a 49% yield of benzoic acid starting from benzophenone. The synthesis has been studied in detail,³⁷ as it offers an electrochemical route to the production of several commercially relevant α -arylpropionic acids, used as non-steroidal anti-inflammatory agents (NSAI).³⁸ A preparative method based on sacrificial electrodes has been set up for the electrocarboxylation of ketones³⁹⁻⁴⁴ and successfully applied to the electrocarboxylation of aldehydes, which failed with conventional systems. The electrocarboxylation of 6-methoxyacetophenone to 2-hydroxy-2-(6-methoxynaphthyl)propionic acid, followed by chemical hydrogenation to 2-(6-methoxynaphthyl)propionic acid (one of the most active NSAI acids), has been developed up to pilot stage.^{40,43} In this case the aluminium salt of the hydroxy acid is soluble in the reaction medium, but precipitates on addition of a number of solvents such as alcohols or ethers. 90% product selectivity was observed in preparative syntheses [up to 40 g of pure 2-(6-methoxynaphthyl)propionic acid produced per run], with a power consumption of the electrochemical stage, as deduced from operative parameters, around 2.7 kW h kg⁻¹.

The influence of the reaction conditions on current and product yields of the electrocarboxylation of acetophenone has been the object of an investigation in our laboratory.⁴⁵ The conditions for lowering the incidence of dimerization to pinacols and optimizing the yield of hydroxy acid are reached at rather negative cathodic potentials, in the range of the second reduction peak of the ketone, at initial ketone concentrations not exceeding 10%, and, quite surprisingly, at rather low flow rates of the electrolyte solution, in the range of laminar flow (Reynolds number up to 500).

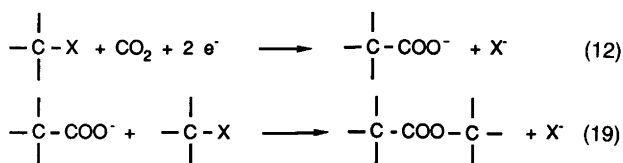
Electrocarboxylation of imines. The first studies on the electrocarboxylation of the $>C=N-$ unsaturation of imines were performed on conventional systems.⁴⁶⁻⁴⁹ A detailed investigation of the electrocarboxylation of a series of substituted aromatic imines⁴⁷⁻⁴⁹ arrived at the conclusion that in most cases the reaction is almost unselective, leading not only to the desired monocarboxylation derivative (i.e. the corresponding N -substituted amino acid) with yields not exceeding 60%, but also to products of monocarboxylation on the nitrogen atom, of dicarboxylation, of carbon-carbon coupling, or of hydrogenation. In contrast, in electrocarboxylation in diaphragmless systems with Al sacrificial anodes,^{50,51} the reaction appears to be more selective, the hydrogenation being almost totally suppressed and the dimerization substantially reduced. Monocarboxylation at the carbon atom and dicarboxylation are the main reactions. The carbamate moiety of the dicarboxylation derivative, in the course of the hydrolysis, decomposes with evolution of carbon dioxide, thus leading to the amino acid, which at the end of the electrolysis is recovered in yields of up to 90% (Scheme 5).



Scheme 5.

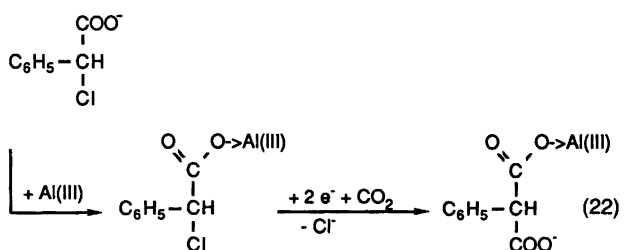
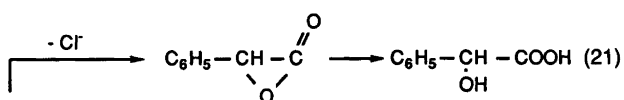
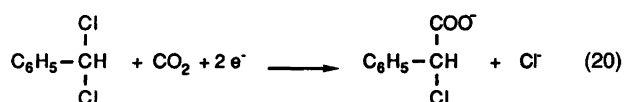
An electrochemical plate and frame cell, with semi-continuous renewal of the particulated Al sacrificial bed, has been recently proposed for the scale-up of electrocarboxylation processes, and successfully used for the carboxylation of benzalaniline.⁵²

Electrocarboxylation of halides. In the last fifty years a large number of studies has been devoted to the electroreduction of organic halides.⁵³ A synthetic approach to the electrocarboxylation of halides came for the first time from Wawzonek⁵⁴ and was later improved by Baizer⁵⁵ making use of conventional diaphragm systems. Alkyl, benzyl and allyl halides are quite easily electrocarboxylated, but it was observed that, in the presence of tetraalkylammonium ions as supporting electrolytes, the carboxylated anion acts as a nucleophile towards the unchanged halide, leading to the corresponding ester (Scheme 6).



Scheme 6.

This reaction appears particularly undesirable in the case of the synthesis of carboxylic acids starting from valuable halides. Bulky halides have quite a slow esterification rate, but in the large majority of cases the reliability of the synthesis is strongly compromised by this follow-up reaction. A considerable improvement of the synthesis came from the use of sacrificial anodes: the formation of complex salts between the carboxylate anion and the metal cations totally inhibits the nucleophilicity of the carboxylic moiety, thus allowing very high conversions of the halide and excellent yields of carboxylated products. This matter has been summarized in several reviews.^{16,56,57} The synthesis has been developed towards the production of some NSAI, starting from the parent halide. Aluminium^{58,59} and magnesium^{60,61} anodes have been used, and the French company SNPE has brought a magnesium-based process up to industrial production.⁶² It is quite interesting to observe that in the case of benzal chloride (Scheme 7) the carboxylation in conventional diaphragm systems failed, leading to poor yields of phenylacetic and mandelic acid⁶³ [reaction (21)]; in contrast the use of an aluminium anode causes carboxylation to take place, because the self-esterification of the first carboxylate anion onto the second chloride group is hindered by the formation of aluminium complex salts⁶⁴ [reaction (22)]. In this way yields of phenylmalonic and chlorophenylacetic acids of up to 30% each are obtained.



Scheme 7.

An interesting procedure in which a nickel-catalysed electrocarboxylation of benzyl halides, precursors of NSAI, is performed with sacrificial zinc or magnesium dispersed as a powder in the anolyte of a two compartment cell, and oxidized on an inert anode, has recently been published.⁶⁵

Nickel complexes have also been used for the electrochemical synthesis of symmetrical ketones, starting from organic halides and carbon dioxide, with magnesium sacrificial anodes.⁶⁶

Conclusions

As has been stressed several times in the course of this concise review, sacrificial anodes used in electrochemical processes involving carbon dioxide, represent more than a mere expedient for the performance of cathodic processes avoiding unwanted anodic reoxidations. Considerable improvements in yields and selectivities and simpler isolation procedures are claimed in the majority of the processes described so far. A criticism of this technology has recently been mounted in some review articles,^{67,68} as it unavoidably produces, after the separation of the products, aqueous solutions containing stoichiometric amounts of salts of the metals used as anodes. Some solutions to this problem are possible: in the case of zinc, as demonstrated by the evaluations of the DECHEMA Institute for the synthesis of oxalic acid,²³ the metal can be electrolytically recovered from the mother liquors; Al(III) or Mg(II) salts can easily be precipitated as hydroxides, recovered by filtration and dehydrated to the corresponding oxides. In this last case the coupling of the hydroxide treatment to existing large-scale electrometallurgical processes such as aluminium production, should not pose technological problems for the quantitative recovery of the metal. It is therefore our opinion that the coupling of cathodic processes to the anodic dissolution of metals could be easily applied to a large number of electro-organic syntheses, not only on a laboratory scale but also to the industrial production of fine chemicals, with moderate outlay for metal recovery on the overall production costs.

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