

Electroorganic CO₂ Fixation Via Paired Electrolysis and Nanoscale Electrocatalysis

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This manuscript was written by Kseniia Medvedeva with critical comments and revisions by Dr. Anna Klinkova and corresponding collaborators. This thesis is based on key projects that have either been published, submitted or are in preparation for peer-reviewed scientific journals. The contributions of all authors are provided below in detail.

(1) Translating Tactics from Direct CO₂ Electroreduction to Electroorganic Coupling Reactions with CO₂

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(2) Electrochemical CO₂ Fixation to α -Methylbenzyl Bromide in Divided Cells with Nonsacrificial Anodes and Aqueous Anolytes

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The contribution of Kseniia Medvedeva includes performing electrochemical experiments, product analysis, and formal analysis. Jury Medvedev performed conceptualization, electrochemical experiments, product analysis, formal analysis, and wrote the manuscript. Feng Li performed DFT calculations. Anna Klinkova designed the project, supervised its execution and manuscript writing.

(3) Sustainable at Both Ends: Electrochemical CO₂ Utilization Paired with Electrochemical Treatment of Nitrogenous Waste

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(6) Synthesis of α -Amino Acids via Electrochemical Fixation of CO₂ to Imines Using Different Metal Cathodes

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Abstract

Sustainable energy driven electroorganic synthesis provides a green and inexpensive alternative to traditional synthetic approaches. For instance, the electroreduction of many classes of organic molecules enables the synthesis of carboxylic acids *via* coupling with CO₂ (electrocarboxylation, EC) that presents a route towards pharmaceuticals and industrially relevant precursors. Historically, the development of EC was performed in undivided systems with sacrificial metal anodes (e.g., Mg). Upon dissolution, metal anodes produce Mg²⁺ ions that may interact with active species produced on a cathode, significantly affecting the reaction mechanism. Despite the high yields of target products achieved on a lab scale, the sacrificial-anode-based systems showed many significant drawbacks preventing them from industrial implementation. To this end, during my Ph.D. program, I aimed to develop an alternative sacrificial anode-free system. Thus, I studied the system and catalyst design for EC paired with useful anodic processes.

In this thesis I discuss the feasibility of EC coupling with sustainable anodic processes (oxygen evolution reaction, ammonia or urea oxidation reactions) and suggest suitable system design. Next, I show the electrocatalyst screening on bulk metal electrodes for the EC of organohalides and imines in the absence of sacrificial metal anodes. Then I elucidate how surface chemistry and morphology of metal nanoparticles affect the EC of organohalides and imines and how stable Au, Cu, and Pd nanoparticles are during these reactions. Finally, I propose EC in a pressurized electrochemical cell towards high EC selectivity even at high organic precursor concentrations.

In Chapter 3, I focus on the EC coupling with oxygen evolution reaction, ammonia oxidation reaction, and urea oxidation reaction. I discuss the disadvantages of the conventional method, perform membrane optimization and the screening of reaction conditions in the new

proposed system. Extensive electrochemical results allowed me to propose the changes in the reaction mechanism in detail. I concluded this chapter with the discussion of the feasibility and energetical benefits of the anodic N-waste treatment (ammonia and urea oxidation reactions). This chapter shows that anion exchange membrane is the only membrane type that allows efficient EC in the absence of sacrificial metal anodes. The experimental observations revealed the need in the optimization of electrocatalyst and system design towards more selective EC at higher precursor concentrations.

In Chapter 4, I aimed to evaluate electrocatalytic activity of bulk materials towards EC of organohalides and imines. I mapped out the relationship between cathode materials and activation of a wide range of organohalides. Additionally, I determined suitable substrates for electrode preparation for EC based on the material inactivity within the EC potential window. I demonstrate that even though there are certain trends for material (in)activity in EC, each organic precursor is unique and catalyst selection needs to be performed carefully. The discussion in this chapter highlights the need to further optimize cathode materials towards higher activity of EC and provides a tool – a map – to continue the cathode optimization in that direction.

In Chapter 5, I discuss the application of nanomaterials as electrocatalysts in EC. I am evaluating nanoparticle electrocatalytic efficiency and structural stability in EC considering factors such as the surface chemistry of the nanoparticles, their surface morphology, and the nature of the material. I discovered that the surface chemistry of nanoparticles has strong effect on the EC selectivity. The effect of the nanoparticle surface features on the EC outcome varied depending on the organic precursor-nanomaterial combination. I found that Pd nanoparticles show great performance in the EC of imines and Cu nanoparticles with developed surface gave almost

quantitative faradaic efficiencies for the EC of organohalides. Pd and most of the Au nanoparticles showed good stability in EC, while Cu nanoparticles underwent severe structural degradation.

In Chapter 6, I show the feasibility of EC at high concentrations of organic precursor with the correct CO_2/RBr ratio in the reaction mixture that was achieved using a pressurized electrochemical cell.

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List of Abbreviations

AA	Ascorbic acid
ACN	Acetonitrile
AEM	Anion exchange membrane
AOR	Ammonia oxidation reaction
BNP	Branched nanoparticle
BPM	Bipolar membrane
CA	Chronoamperometry
CC	Core-cage nanoparticle
CCS	Carbon capture and sequestration
CCU	Carbon capture and utilization
CEM	Cation exchange membrane
CG	Cage nanoparticle
CP	Chronopotentiometry
CPC	Cetylpyridinium chloride
CTAB	Cetyltrimethylammonium bromide
CTAC	Cetyltrimethylammonium chloride
CV	Cyclic voltammetry
DFT	Density functional theory
EC	Electrocarboxylation
ECSA	Electrochemically active surface area

EDG	Electron donating group
EDX	Energy dispersive X-Ray analysis
EWG	Electron withdrawing group
FE	Faradaic efficiency
FID	Flame ionization detector
GC	Gas chromatography
HER	Hydrogen evolution reaction
LSV	Linear sweep voltammetry
LE	Ligand exchange
NaSal	Sodium salicylate
NC	Nanocube
NMR	Nuclear magnetic resonance
NP	Nanoparticle
NS	Nanosphere
OER	Oxygen evolution reaction
QRE	Quasi-reference electrode
RL	Raspberry-like
scCO ₂	Supercritical carbon dioxide
SEM	Scanning electron microscopy
SLA	Sodium L-ascorbate
TBA	Tetrabutylammonium
TCD	Thermal conductivity detector

TEA	Tetraethylammonium
TEM	Transmission electron microscopy
TLC	Thin-layer chromatography
UOR	Urea oxidation reaction
UPD	Underpotential deposition
XRD	X-ray diffraction analysis
XPS	X-ray photoelectron spectroscopy
α -AA	α -amino acid

Chapter 1 Introduction

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Contribution: assisted with manuscript writing.

1.1 Utilization of CO₂

Climate change is a major concern of the 21st century that is predominantly driven by greenhouse gas emissions. The continuous increase in global temperatures (Figure 1.1a) is strongly connected to the consistent rise of atmospheric CO₂ concentrations (Figure 1.1b) since the start of industrialization in 1750. Compared to pre-industrial times, current CO₂ levels are ~130% greater due to constant anthropogenic emissions.² To support climate change mitigation and the implementation of preventative measures globally, the Paris Agreement was adopted by 196 parties on December 12th, 2015, during the 21st United Nations Climate Conference (also known as Conference of Parties, COP21). The goal of this agreement was to keep “the increase in the global average temperature to well below 2 °C above pre-industrial levels” to ultimately “limit the temperature increase to 1.5 °C above pre-industrial levels”.³ To this end, decreasing CO₂ emissions by developing CO₂ capture and utilization technologies is an international climate action goal.

At present, there are four widespread strategies to reduce CO₂ emissions. Two aim to directly decrease CO₂ emissions through improving process energy efficiency and changing to renewable energy sources. The other two focus on CO₂ utilization or isolation from the atmosphere through Carbon Capture and Utilization (CCU) and Carbon Capture and Sequestration (CCS), respectively. CCS captures CO₂ from large point sources and sequesters this greenhouse gas into a natural sink while CCU captures and converts CO₂ into value-added products.¹

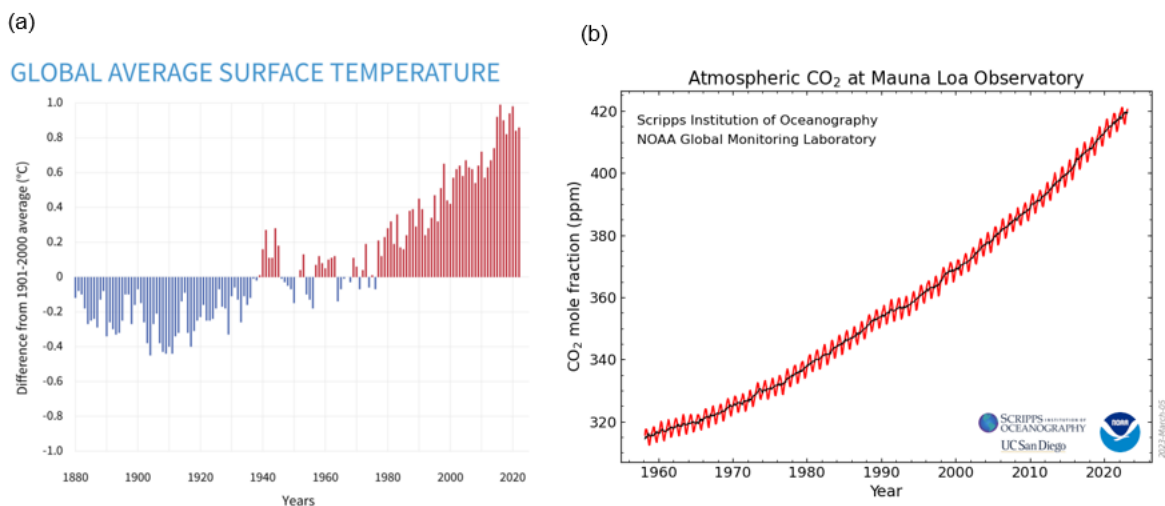


Figure 1. 1: Correlation of the global surface temperature increase and CO₂ emissions. (a) Average global surface temperature compared to 20th century average. NOAA Climate.gov graph⁴ (b) atmospheric CO₂ concentration obtained at an altitude of 3400 m in the northern subtropics.⁵ Images provided by NOAA Global Monitoring Laboratory, Boulder, Colorado, USA (<https://gml.noaa.gov>)

The CO₂ utilization pathways part of the CCU strategy may be designated as either physical or chemical processes (Figure 1.2).⁶ Physical CO₂ utilization involves using the CO₂ gas directly without altering the chemical composition of this molecule, for instance, in carbonated drinks, dry ice, fire extinguishers or algae farms. Additionally, CO₂ can be used as an additive to indirectly enhance large scale processes such as oil recovery, gas recovery, and geothermal systems. In contrast, chemical CO₂ utilization uses this molecule as a feedstock for the synthesis of chemicals and fuels. CO₂ can be broken down to carbon or CO, reduced to various C1 molecules, and reacted with other molecules to form new C-C bonds under applied heat/pressure/potential. Out of all the implemented CO₂ abatement pathways, urea synthesis and inorganic carbonate formation consume the highest amounts of CO₂ by utilizing 114 Mt/y and 50 Mt/y, respectively.⁷ Other areas of CO₂ utilization show substantially lower usage, contributing to a total CO₂ consumption rate of only ~200 Mt/y.⁷ This amount of CO₂ consumed is significantly lower than the yearly anthropogenic CO₂ emissions ($\geq 30\,000$ Mt) thus, highlights the need to decrease CO₂ emissions and implement novel CO₂ utilization technologies.⁸

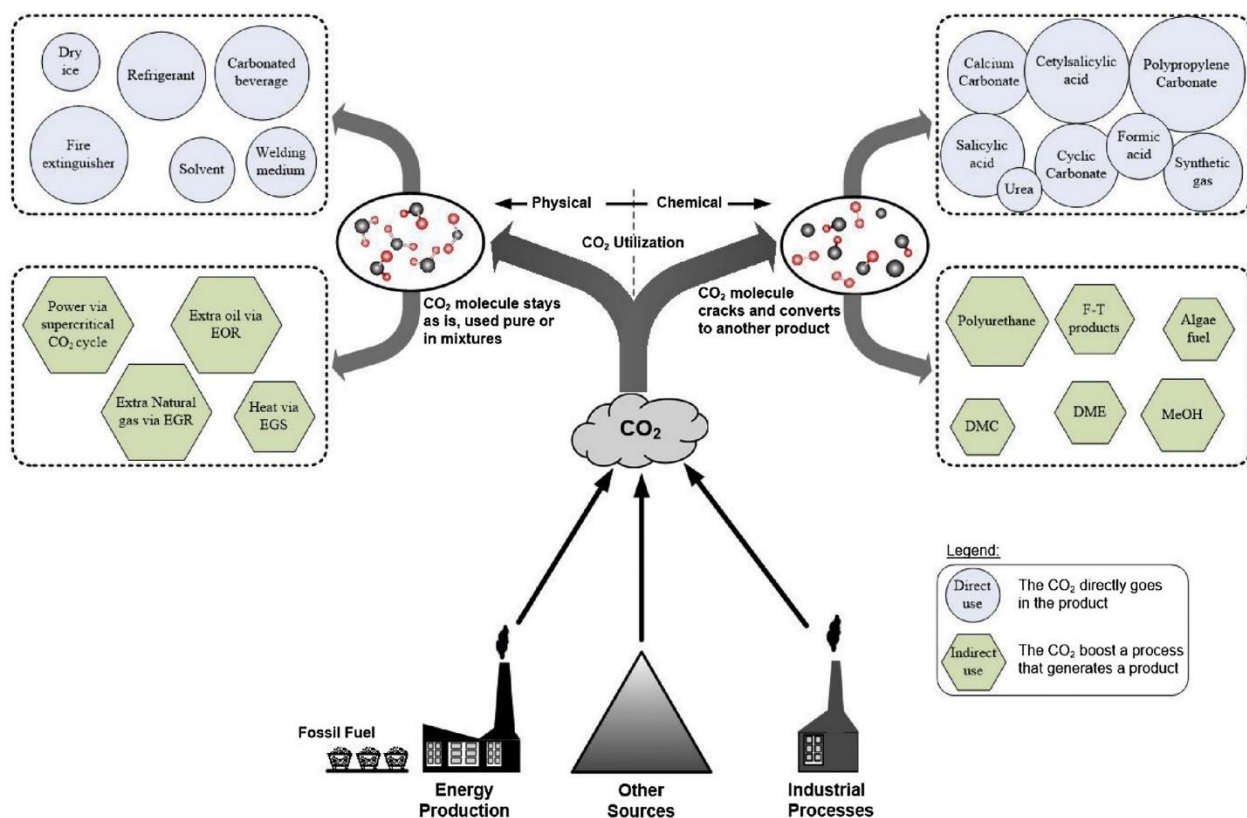


Figure 1. 2: Schematic showing pathways for CO₂ utilization. Reprinted with permission from ref [6]. Copyright 2018 Elsevier.

Emerging electrocatalytic technologies for the sustainable production of value-added chemicals that can simultaneously serve as a long-term energy storage solution for renewable electricity are currently on the rise.^{9,10} These developments have been stimulated by multiple global initiatives to mitigate climate change and the declining prices of renewable electricity. In the past decade, the prices of solar and onshore wind electricity decreased by 89 and 70%, respectively, allowing for the installation of new solar and wind plants that are more profitable than a new average coal plant.¹¹ One of the most prominent and rapidly advancing sustainable electrosynthesis technologies is the electroreduction of CO₂ to fuels and chemicals. This technology serves as a CO₂ utilization strategy that benefits from the aforementioned renewable energy resources.

Research efforts are focused on direct CO₂ electroreduction in aqueous media to single and multicarbon products. To date, substantial progress has been made in the field targeting industrially relevant current densities, high faradaic efficiencies, and exceptional selectivity.¹² The scope of

products that can be formed, however, is mostly limited to CO as well as the mixtures of simple hydrocarbons, acids, and alcohols.¹³ Notably, studies on the products containing C₃₊ carbon chain are very limited.

1.2 Electrocarboxylation reaction

In addition to direct CO₂ reduction to single- and multi-carbon products, CO₂ can also be electrochemically coupled with various organic precursors to yield a wide range of value-added carboxylic acids and esters, α -amino acids and their derivatives, α -hydroxy/methoxy/thiomethoxy acids and their derivatives, cyclic carbonates and carbamates, and polycarbonates. Notably, this EC approach can afford chiral carboxylic acids,^{14,15} essential for correct biological activity in anti-inflammatory and other drugs. A few examples of organic carboxylation products that are important pharmaceuticals or precursors for chemical and polymer industry are shown in Figure 1.3.

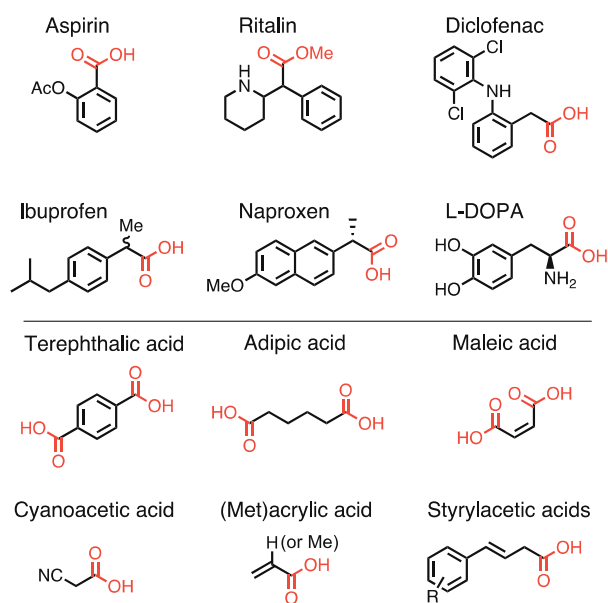


Figure 1. 3: Examples of industrially important carboxylic acids: pharmaceuticals (top) and intermediates for chemical and polymer industry (bottom). Reprinted with permission from ref. [321]. Copyright 2021, Royal Society of Chemistry.

Many carboxylation products are currently produced unsustainably: for example, industrial methods of producing Naproxen still show low atom economy (Figure 1.4a,b). Greener synthetic alternatives that rely on conventional heterogeneous and homogeneous catalysis are available or being developed for some carboxylic acids (e.g., Figure 1.4c).¹⁶ Electrochemical synthetic routes to carboxylation products where CO₂ is used as a C1 synthon are being suggested now increasingly

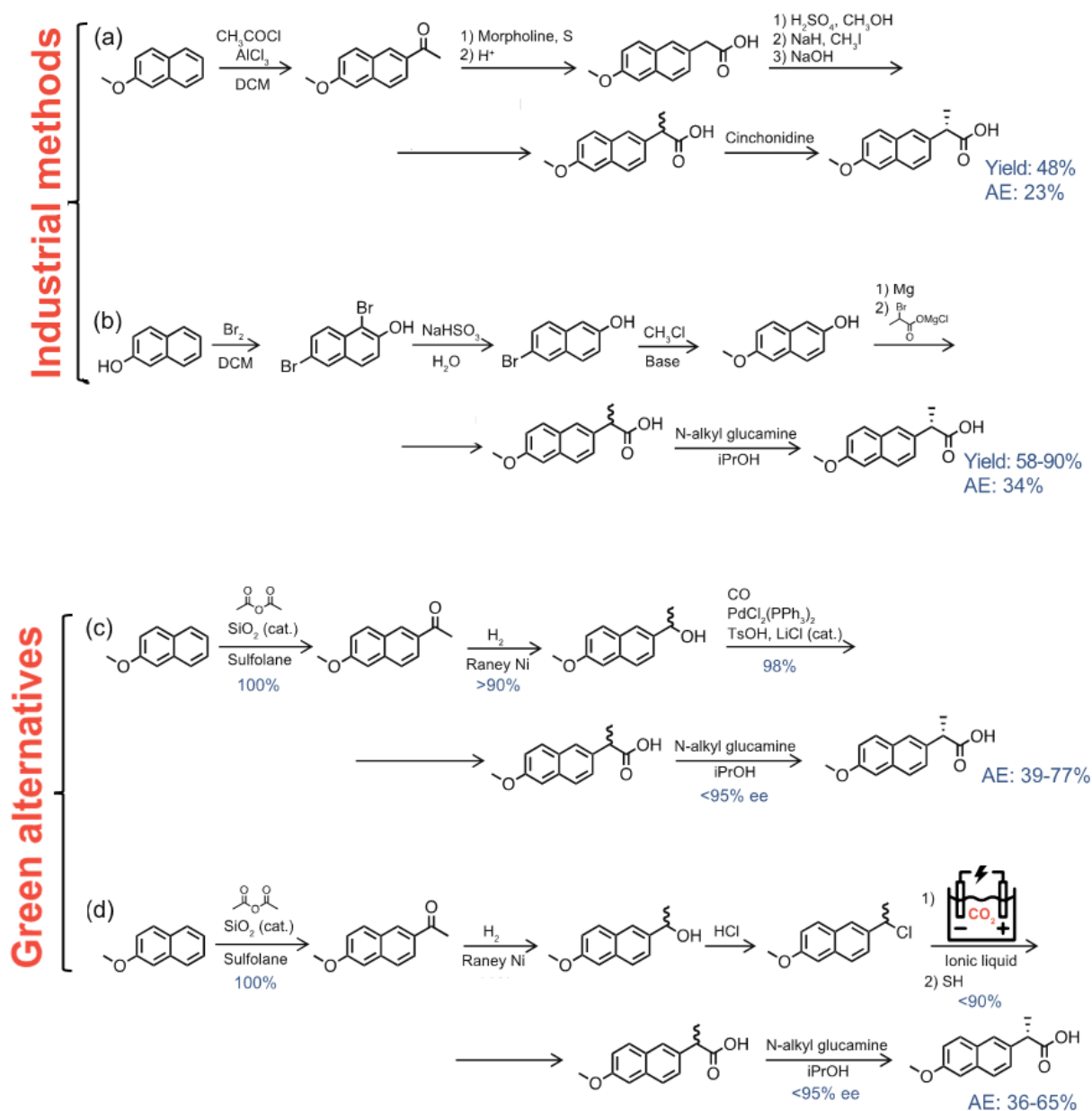


Figure 1. 4: Synthetic routes to Naproxen: (a) patented in 1969 and used by Syntex; (b) patented in 1972 and 1976 and used by Syntex, with initial yields of 58% and 66%, respectively, and improved to 90% yield by 1993; (c) proposed by Shaw and Schlitzer in 2015,¹⁸ (d) reported by Mena et. al in 2020.¹⁶ Isolated yields are shown for the overall industrial routes and for individual steps of proposed routes. AE: atom economy. Reprinted with permission from ref. [321]. Copyright 2021, Royal Society of Chemistry.

(e.g., Figure 1.4d, 1.5a). This growing interest aligns with the renaissance of electroorganic synthesis that has been on the rise since 2000s.¹⁷

Considerable fundamental work on electroorganic synthesis was conducted in the last quarter of the 20th century but slowed down in the 1990s (Figure 1.5b). Although a number of

organic electrosynthesis processes were commercialized, for example, production of adiponitrile (Monsanto),¹⁹ phthalide (BASF),²⁰ and 3,6-dichloropicolic acid (Dow Chemical Company),²¹ electroorganic synthetic methods often are not economically competitive with conventional – albeit less sustainable – synthesis pathways. The recent drive to minimize chemical manufacturing emissions, decrease in sustainable electricity cost, and the developments in electrocatalysis and related nanotechnology all paved the way for current opportunities for further development and, subsequently, more widespread industrial implementation of organic electrosynthesis.²²

While organic electrosynthetic processes are significantly smaller in scale compared to mature inorganic electrosynthetic production (chloro-alkali, aluminum), their implementation has the potential for sustainability improvements in the production of many chemical products.^{23,24} When it comes to electroorganic synthesis that incorporates CO₂ fixation, it is worth noting that it will unlikely consume a substantial amount of CO₂ emissions from the atmosphere.^{25–28} However,

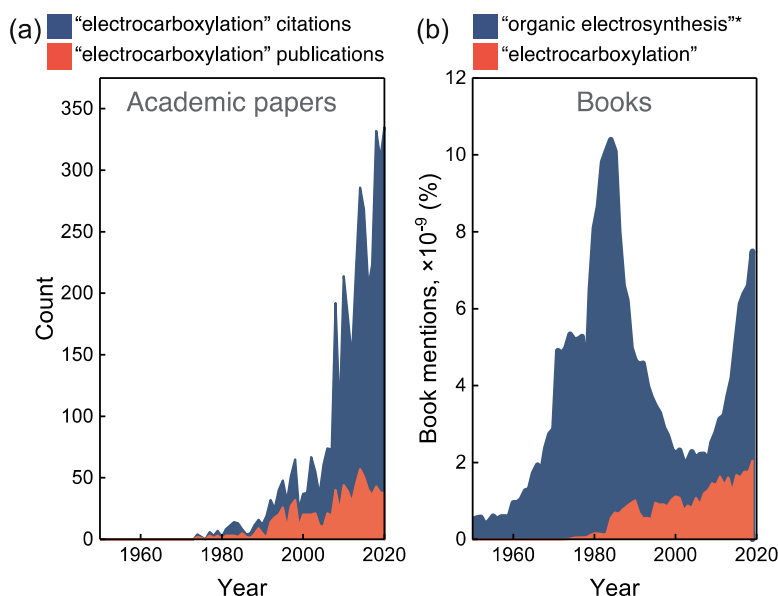


Figure 1. 5: Timeline of electrocarboxylation literature mentions since 1950s. (a) Number of published papers and citations in the Web of Science database on “electrocarboxylation”. Papers include journal articles, reviews, proceedings and meeting abstracts. (b) Ngram data on word mentions in published books (Google Books Ngram Viewer).²⁹ *Mentions of “organic electrosynthesis” also include “electroorganic synthesis” and “organic electrochemical”; mentions of “electrocarboxylation” include only single-word mentions. Reprinted with permission from ref. [321]. Copyright 2021, Royal Society of Chemistry.

it is still relevant to use CO₂ in chemical industry as an easily available and sustainable carbon source, making better use of energy and carbon.

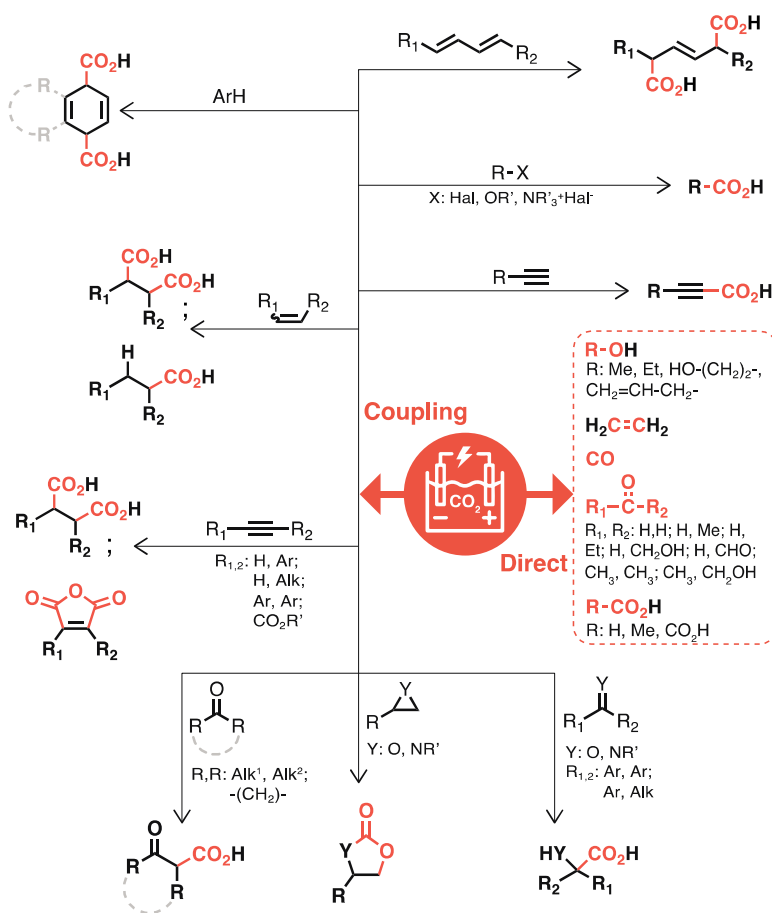
Currently, there remains a lot of work to be done in the field of electroorganic CO₂ fixation to optimize reaction energy requirements, selectivity and product yields before this technology reaches maturity to successfully compete with current industrial methods of chemical synthesis. Specifically, large energy barriers associated with CO₂ utilization in general (including electrochemical, photochemical, and conventional catalysis) are among the main reasons for the majority of industrial methods to produce carboxylic acids and their derivatives rely on alternative methods (e.g., carbonylation of alcohols, oxidation of alkyl groups, etc.). These challenges necessitate the development of efficient catalysts and reaction environments that would minimize the energy requirements and maximize the target product yields, similarly to the challenges faced by the field of direct CO₂ electrolysis into single- and multicarbon products. Because electrocarboxylation (EC) belongs to the realm of organic electrosynthesis, there is an apparent disconnect between the EC studies and some of the successful research tactics becoming increasingly adapted by the direct CO₂ electroreduction community.

1.3 EC: scope of products

Carbon dioxide can be electrochemically coupled with olefins, alkynes, carbonyls and organohalides to yield carboxylic acids and esters, α -amino acids and their derivatives, α -hydroxy, methoxy, thiomethoxy acids and their derivatives, cyclic carbonates and carbamates. Figure 1.6 summarizes EC product classes, as well as products of direct CO₂ electroreduction. Depending on the electrocatalyst nature and reaction parameters, direct CO₂ electroreduction in aqueous media leads to the formation of simple alcohols, hydrocarbons, carboxylic acids, carbon monoxide and complex mixtures thereof, and is generally accompanied by competing hydrogen evolution reaction.³⁰⁻³² In contrast, in aprotic media the product scope is limited to CO and oxalate.³³ As EC involves coupling of CO₂ with a large variety of precursors, by its nature, it is characterized by a much wider scope of possible products compared to CO₂ electroreduction. When CO₂ is coupled to organic halides, the range of EC products include aliphatic,³⁴ benzylic,³⁵⁻³⁸ aromatic,³⁹⁻⁴³ and heteroaromatic^{44,45} monocarboxylic acids. In these reactions, a new C-CO₂H bond is formed in place of the C-Hal (Hal = F, Cl, Br, I) bond. Similarly, in the case of EC of quaternary ammonium salts,⁴⁶ diazonium salts,⁴⁷ and diacetates,⁴⁸ the C-N or C-O bond breaking is followed by the formation of a new C-CO₂H. Generally, EC of alkenes yields dicarboxylic acids,⁴⁹⁻⁵¹ while in the case of Michael acceptors a dominant formation of monocarboxylation products was reported.⁵² Similar to alkenes, the reduction of conjugated dienes leads to dicarboxylation products.⁵³⁻⁵⁵ The outcome of EC of alkynes depends on the structure of the organic substrate and reaction conditions: the formation of propionic acid derivatives was reported for terminal alkynes at Ag cathodes,⁵⁶ while EC of alkynes in the presence of a co-catalyst led to the formation of di- and tricarboxylation products in a form of anhydrides.⁵⁷ Besides alkenes and alkynes, the unsaturated bonds of polycyclic arenes can participate in EC leading to breaking of the aromatic structure and the formation of corresponding dicarboxylic acids.⁵⁸ In addition to the unsaturated C-C bonds and C-X bonds (X = O, N), double C=X (X = O, N) bonds of aromatic ketones⁵⁸⁻⁶¹ and imines⁶²⁻⁶⁴ can also be carboxylated with the formation of α -hydroxy and α -aminocarboxylic acids. Notably, EC of aliphatic ketones does not yield the addition product and result in β -oxocarboxylic acids as a major product instead.

While all the aforementioned EC reactions proceed with the formation of a new C-C bond, electrochemical coupling of organic precursors with CO₂ can also proceed with a formation of C-

The reactivity of different substrates is strongly dependent on their structure and the nature of substituents, which is further discussed below in section 1.4.



10

1.4 Mechanism of EC

In any electrochemical reaction, the electron transfer at an electrode surface occurs between two limiting scenarios: in the first limiting case, the electrode surface is intimately involved in the mechanism of the electron transfer and acts as a catalyst in the reaction; in the second limiting case, the electrode is completely inert, and a redox process occurs via outer-sphere electron transfer between the substrate and the electrode (Figure 1.7a).⁶⁸ In the latter case, the reaction mechanism and kinetics are independent of the electrode material, whereas in the case of an electrocatalytically active cathode, the products, mechanism and kinetics of the reaction are highly dependent on the composition and atomic structure of the electrode material, meaning that small variations can be extremely significant in determining the onset potentials and the outcome of the reaction. For CO₂ electroreduction, the decrease of overpotential, control over the product selectivity and suppression of hydrogen evolution side reaction through new electrode materials is a subject of intense investigation, as small efficiency gains will translate into large cost savings when these processes are scaled up.^{69,70}

In organic electrosynthesis, most studies to date have been on the uncatalyzed electron transfer, represented by a rich body of literature where the reactivity of different functional groups and the effects of substituents is assessed experimentally or computationally. Typically, a single electron transfer and the associated Gibbs free energy is estimated from measured half-peak potentials, which correspond to the potential at half the maximum current in the cyclic voltammetry curve. The values of solution-phase redox potentials for a single electron transfer can also be theoretically calculated using molecular density functional theory (DFT) with B3LYP or M06-2X functionals in the Gaussian package,^{71,72} which generally give satisfactory correlation with theory despite the well-documented drawbacks of DFT in describing the electronic structure of forming radical anions.^{73,74} Roth et al. reported both measured and calculated half-peak potentials for over 180 common organic molecules for photoredox catalysis,⁷⁵ which provided a solid framework for the mechanistic understanding of reductive organic electrosynthesis. Overall, the reduction potentials are highly depended on the organic substrate class and on the nature of substituents in the molecule. In terms of general trends, anhydrides and sulfonyl chlorides show the least negative reduction potentials followed by aromatic halides, ketones and aldehydes, while the reduction of esters, aliphatic halides, nitriles and imines is associated with the highest energy

requirements. Moreover, the presence of a strong electron-withdrawing group in the vicinity of the reaction center in a molecule tends to result in a significant positive shift in the reduction potential, which can be associated with an additional stabilization of the negatively-charged reaction intermediates.

When the cathode is more intimately involved in the reaction (inner sphere electron transfer), the participating redox sites become connected by a chemical bridge and the reaction is catalyzed. In this case, the reduction potentials can be drastically reduced, and different species can have largely varied onset potential differences depending on what cathode material is used. While this catalyzed approach has the potential to offer an unsurpassed tunability of the reaction mechanism, the general catalytic trends for EC are currently poorly understood, due to a large number of catalyst - organic substrate combinations.

In both uncatalyzed and catalyzed scenarios, EC can proceed either via the electrochemical activation of an organic substrate which subsequently reacts with CO₂, or via electrochemical activation of CO₂ itself, which then reacts with the organic substrate. We can consider this in greater detail on the example of EC of organohalides. In the literature, the reaction pathways are generally presented in terms of the molecular steps involved (Figure 1.7b). While being sufficient for the uncatalyzed scenario, this description oversimplifies the mechanistic picture when a catalyzed process takes place. Specifically, different reaction steps occur either at the electrode surface or in the electrolyte without the participation of the electrode surface (Figure 1.7c). This distinction is important, as some metal surfaces can potentially catalyze one of the EC pathways, but not the other, introducing a variation in the mechanisms and associated energy barriers. While computational models for molecular (uncatalyzed) steps are quite reliable as discussed above, there is currently a lack of computational studies that consider catalyzed surface reactions at the cathode, associated with the complexity of modelling carbocations and computing inner sphere electron transfer in aprotic media in solid-state DFT packages. Recently, we were able to compare the energy barriers for the initial activation of an organohalide and CO₂ at Ag (111) surfaces during the first electron transfer using VASP package, which described the switch in the preferential reaction pathway with increasing voltage (Figure 1.7e); however, the computational model was insufficient to describe the second electron transfer leading to the formation of a carbanion.⁷⁶ The development of reliable DFT methods for accurately describing surface-catalyzed molecular

reduction processes in aprotic media is necessary for further clarification of reaction mechanisms of EC and electroreductive organic synthesis more generally.

Another general mechanistic intricacy of EC is associated with the commonly used counter electrode reaction: the dissolution of sacrificial Mg, Al or Zn anodes.⁷⁷⁻⁷⁹ The main advantage of this approach is that the anodically formed metal ion stabilizes the cathodically formed carboxylate ion, preventing its reaction with the unreacted organic precursor, which leads to better target product yields.⁸⁰ From the mechanistic perspective, the presence of consumable anodes can lead to the product being formed as a result of multiple simultaneous reaction pathways, including *in-situ* formation of Grignard reagent (Figure 1.7d). In the catalyzed EC, this convoluted mechanistic description of the process complicates the design of efficient heterogeneous electrocatalysts for this reaction.

With respect to side reactions and selectivity in the catalyzed EC, first of all, at a given potential, the electrocatalyst can either catalyze the reduction of the organic precursor, the

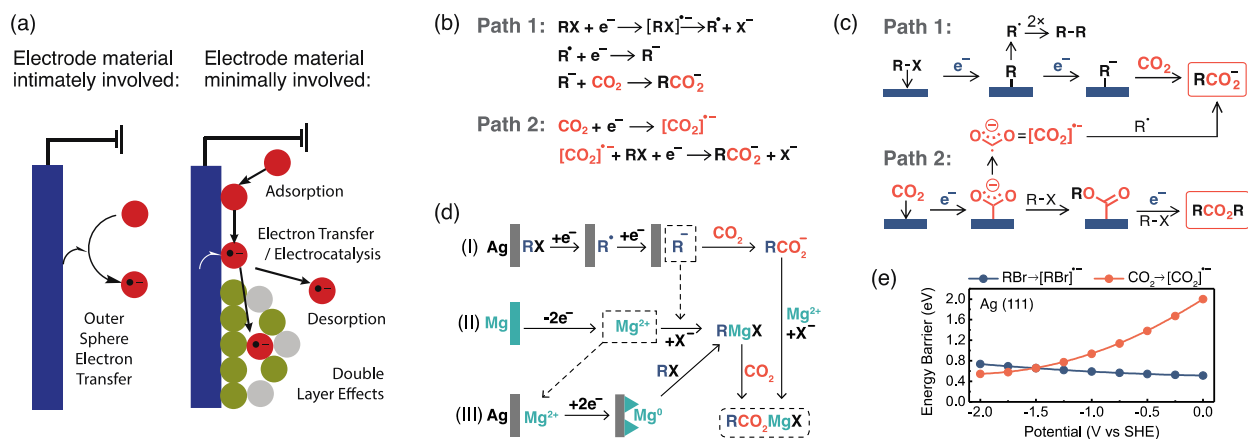


Figure 1. 7: Mechanistic descriptions of EC. (a) Two limiting cases for electron transfer; adapted from ref [68] under CC-BY 4.0. Published by John Wiley and Sons (b) Non-catalyzed EC pathways. (c) Catalyzed EC pathways. (d) Participation of sacrificial Mg anode in Ag-catalyzed EC: carboxylate stabilization only (I), stabilization of electrochemically formed carbanion with a formation of Grignard reagent (II), and electroreduction of Mg^{2+} to Mg^0 and subsequent chemical formation of Grignard reagent (III).⁷⁶ (e) DFT calculations of energy barriers for the first electron transfer to α -methylbenzyl bromide and to CO_2 on Ag(111) cathode surface.⁷⁶ Reprinted with permission from ref. [321]. Copyright 2021, Royal Society of Chemistry.

reduction of CO₂, or both. When the precursor reduction is preferentially catalyzed, it leads to the formation of a corresponding radical (1e⁻ reduction) and/or a corresponding anion (2e⁻ reduction, or two sequential 1e⁻ reductions). The formation of radicals can lead to their coupling, yielding dimeric organic molecules without the incorporation of CO₂ as a side product. The formation of reactive carbanions generally favors EC, but due to being strong bases and good nucleophiles, they are sensitive to the presence of any proton donors and can also participate in substitution reactions with the initial organic substrate. When CO₂ reduction is catalyzed, a direct CO₂ electroreduction is a competing process to EC, generally yielding CO as an undesirable side product. Thus, for a given electrocatalyst – organic substrate combination, it is important to consider whether the 1e⁻ and 2e⁻ reduction of the organic substrate and CO₂ electroreduction occurs at overlapping potentials, as this leads not only to a convoluted EC mechanism but also to decreased current yields of target products.

1.5 Cathode materials

In EC, as in any electrosynthesis, the electrode material is a key reaction parameter as it determines the kinetics and thermodynamics of electron transfer. Unfortunately, in contrast to some common inorganic electrosynthetic processes (e.g., hydrogen and oxygen evolution reactions, CO₂ electroreduction), in organic electrosynthesis the choice of the electrode material is often empirical and a rationale for a successful reaction outcome is therefore unknown. Figure 1.8a shows the most commonly used electrodes in electroorganic synthesis in the past two decades.⁶⁸ Carbon-based materials, predominantly glassy carbon, graphite, and boron-doped diamond, are the most commonly used as electrodes in such transformations. In the past, mercury was a common go-to cathode due to its high hydrogen overpotential and liquid state that allowed it to readily regenerate its surface, although in 2000s mercury has been mostly abandoned due to its toxic nature. Currently, platinum is another common option due to its robustness and redox stability.

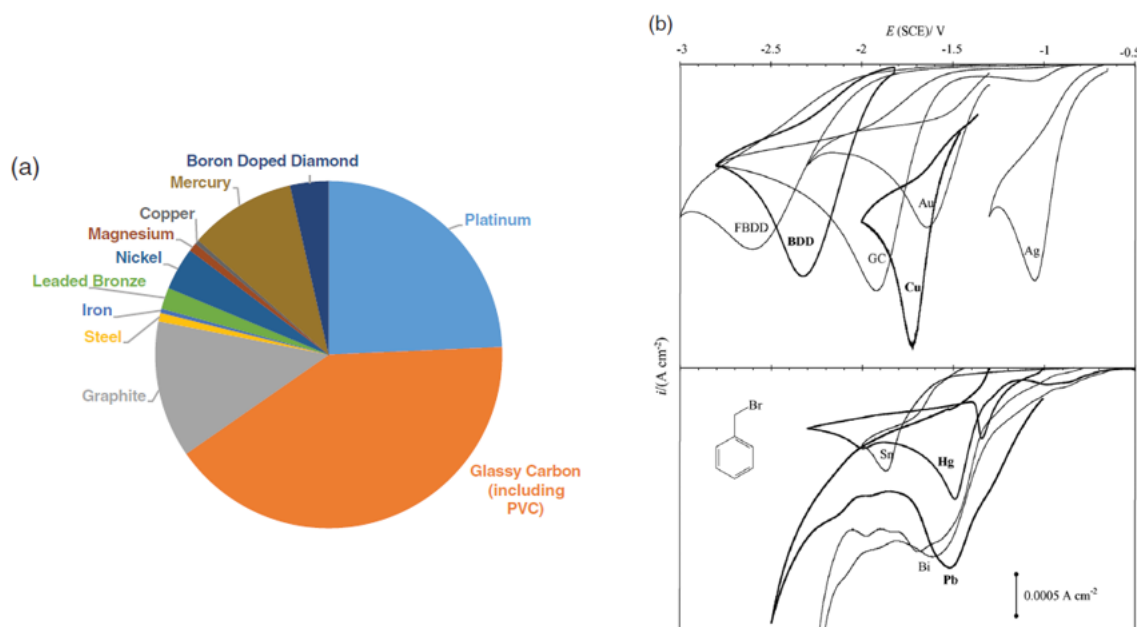


Figure 1. 8: Cathode materials in electroorganic synthesis. (a) Occurrence of electrode materials used (cathode or anode) in a survey of 915 synthetic electroorganic protocols published between 2000 and 2017; adapted from ref [68] under CC-BY 4.0: under CC-BY 4.0. Published by John Wiley and Sons (b) Performance of a series of cathodes in electroreduction of benzylbromide in an aprotic medium,⁸¹ reproduced with permission from ref. [81], Copyright 2005, Elsevier.

Also, Pt is more likely to behave as an electrocatalyst, in contrast to a glassy carbon or graphite electrode that typically favor outer sphere electron transfer. Many other metals and metal combinations, both in the form of polycrystalline and nanostructured materials, have also been reported in electroreductive organic transformations, although such examples are less common, and systematic studies of their relative performance are lacking.

Many studies of electrodes for electroreductive activation of organic molecules have been performed in the absence of CO₂, although the discovered trends are relevant for EC as well. However, the comparative analysis of common polycrystalline metal cathodes has been generally performed to establish the activity dependence for a 1e⁻ reduction of organohalides,^{82,83} and not for the 2e⁻ reduction relevant for EC. To date, the most explored area in cathodic organic chemistry and specifically EC is reductive activation of organohalides. Generally, Ag shows a superior catalytic activity in organohalide reduction among single-metal cathodes (Figure 1.8b),⁸² which has been attributed to a strong halide (especially bromide and iodide) affinity to this metal.^{82,83} Nanostructuring advantage was demonstrated both in terms of increased active surface area and intrinsic activity: e.g., Ag nanorods have a 0.1 V lower peak potential compared to bulk Ag,⁸⁴ although the reasons behind this superior performance require further studies. Alloying, both for Ag-based and other metals (e.g., Ag-Cu,⁸⁵ Pd-Cu⁸⁶), has also been reported to have a positive impact on the electrocatalytic activity in organohalide activation, which has been attributed to synergistic effects of the metals, although the active sites and specific mechanisms of activation have not been identified. The influence of support materials on Ag nanoparticles performance in benzyl bromide reduction was also demonstrated, with some supports resulting in a positive shift in the reduction peak.⁸⁷ Another interesting aspect requiring further studies is the stability of a cathode surface in the course of EC, especially for nanostructured materials: it was recently found that Ag nanoparticles, while being more active, exhibit structural degradation associated with particle coalescence and dissolution during organohalide reduction.⁸⁸ Thus, further studies should be focused on finding the right balance between maximizing intrinsic activity and stability in the electrocatalyst design.

1.6 Cell parameters and configurations

While identifying the electrocatalyst active sites is probably the most desirable solution to maximizing reaction selectivity, choosing an appropriate electrolyte, cell design and reaction parameters is another common approach to maximize desired product yields and circumvent the problem of side reactions. The specificities of the EC reaction mechanism dictate certain requirements for the availability and relative concentrations of the organic precursor and CO₂. Specifically, when the anion formation is a result of two single-electron transfers, the concentration of the organic precursor cannot be too high, otherwise radical coupling⁸⁹ would dominate over the second electron transfer. When carbanions are formed, the concentration of CO₂ has to be high, i.e., it should be omnipresent at the electrode surface to minimize the reaction of the carbanions with species other than CO₂. Considering that the concentration of CO₂ is limited by its solubility in the electrolyte, pressurized reactors, supercritical CO₂, and ionic liquids with high CO₂ solubility are advantageous for maximizing EC yields.

According to Henry's law, the solubility of CO₂ in organic solvents is increased with increasing pressure, making high-pressure electrochemical cells attractive for EC. A positive effect of the CO₂ pressure on the reaction efficiency and selectivity has been demonstrated for EC of styrenes and organic halides.^{90,91} Moreover, using high CO₂ concentration enables EC of concentrated solutions of organic substrates, thereby minimizing the quantities of solvents and electrolytes needed for this reaction.⁹⁰ Supercritical carbon dioxide (scCO₂) can also be employed for EC, serving both as a reagent and a reaction media.⁹² In this case, a small amount of an organic co-solvent with conductive salts or ionic liquids are required as electrolytes. The use of scCO₂ was found to be especially efficient for EC of polycyclic aromatic compounds: this approach led to a several fold-increase in the target product yields compared to the reactions in acetonitrile under atmospheric pressure of CO₂. Similarly, EC of organic halides and ketones in scCO₂ was also found to proceed efficiently.⁹³

In contrast to common aprotic organic solvents (acetonitrile, dimethylformamide) used for electroorganic synthesis in combination with conductive organic salts, ionic liquids (ILs) possess intrinsic conductivity, higher CO₂ solubility and low toxicity, are stable and non-flammable, which makes them an attractive media for EC.⁹⁴ Reported to date EC of various classes of organic compounds, including organic halides,⁹⁵⁻⁹⁷ ketones,^{98,99} epoxides¹⁰⁰ and activated olefins¹⁰¹ in ILs

showed promising results. Besides higher yields of EC products in ILs, a lower contribution of competing side reactions was observed due to an additional stabilization of charged intermediates and their longer lifetimes in this charged environment.

As electrosynthesis implies pairing of reduction and oxidation reactions, it is important to consider whether and how the anodic process affects cathodic EC in various cell configurations. In this regard, when it was first reported,¹⁰² EC was conducted in solutions of quaternary ammonium salts in a two-compartment cell divided by a diaphragm with a mercury cathode and a platinum anode, where oxidation of bromide ions from the electrolyte took place. This initial patent on the EC of 1,3-butadiene was followed by a number of reports on EC of olefins, alkynes and

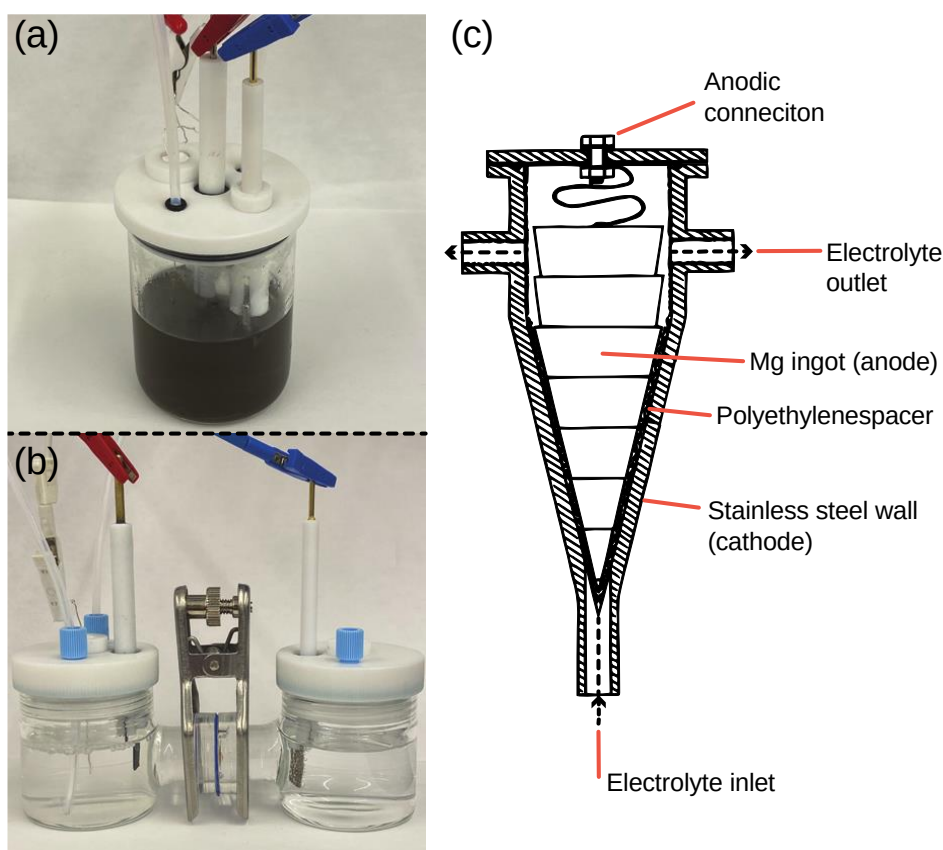


Figure 1. 9: Cell configuration examples. (a) EC of α -methylbenzyl bromide in an undivided electrochemical cell with a Mg sacrificial anode.⁷⁶ Photos provided by the Klinkova lab. (b) EC of α -methylbenzyl bromide in a divided cell with two compartments separated by an anion exchange membrane and urea electrooxidation as an anodic process.¹⁰⁹ (c) A V-shaped “ingot eating” pressurized electrolytic cell based on a consumable Mg anode used for multi-kg-scale EC;^[110] adapted with permission from ref. [110], Copyright 1989, Springer.

aromatic ketones in divided cells, with yields of carboxylic acids not exceeding 50% due to the formation of an ester via the nucleophilic attack of the unreduced organic substrate by the carbanion intermediate. Since the 1970s, sacrificial anode-based undivided cells were preferred over the two-compartment configuration due to much more favorable product yields.¹⁰³⁻¹⁰⁵ While providing stability of the reaction intermediates and, thus, showing high product yields, the latter method has a few significant drawbacks. First, low atom economy of this process due to the use of stoichiometric amounts of metal represents a serious problem in terms of the process sustainability, defeating the major purpose of introducing electrocatalysis into chemical production. Furthermore, the presence of not only metal ions but also metal particulates (Figure 1.9a) lowers the product purity and introduces additional steps for its purification. Lastly, the reliance of this method on a gradual consumption of the anode presents challenges in terms of the reaction scale up.¹⁰⁶ Although the technical feasibility of EC scale-up from 30 mL atmospheric pressure laboratory cell to a 400 L pressurized pilot plant (operating at 1000 A current) was demonstrated by relying on the use of a massive consumable anode moving toward the cathode during electrolysis, this complicated approach (Figure 1.9c) does not address the other downsides of using sacrificial anodes. Recently, sacrificial anode-free EC approaches have started gaining increasing attention to circumvent these challenges,¹⁰⁷ e.g., by performing convergent paired electrolysis in an undivided cell,¹⁰⁸ or by introducing a useful process at the anode in a divided cell with different electrolytes and dividing ion exchange membranes (Figure 1.9b).¹⁰⁹

1.7 Pathways for EC reaction optimization

Over the past decade, substantial progress has been achieved in understanding factors controlling the efficiency and selectivity of CO₂ electroreduction. The major efforts have been focused on understanding and developing efficient heterogeneous electrocatalysts, which are the core of this technology. Combining experimental and theoretical studies has proven to be a successful strategy for catalyst optimization and elucidation of the nature of active sites, yielding a framework to understand catalytic trends and tailor a rational development of improved catalysts, as well as to uncover broader governing principles that are applicable to other emerging and promising clean energy reactions.¹¹¹ Similar catalyst design strategies aiming to increase the number of active sites and their intrinsic activity have been previously developed for hydrogen and oxygen evolution reactions. Now, following a successful transfer of these approaches to CO₂ electroreduction and their further improvement, they are being adapted in nitrogen electroreduction research. Similar transferability is applicable to EC and other reductive electrosynthetic reactions, not only in terms of the catalyst optimization strategies, but also in terms of the reaction environment, electrolyzer and general system design approaches developed in CO₂ electroreduction and other adjacent fields.

The CO₂ electroreduction benefited from systematic studies of the effect of electrocatalyst materials on the reaction mechanism and product selectivity. Due to the detailed understanding of the reaction mechanisms supported by experimental ex- and in-situ techniques, DFT analysis of binding energies for the key reaction intermediates has been used to map out the selectivity of different metals towards different reaction pathways. For example, Figure 1.10a illustrates a method for predicting product distribution of CO₂ electroreduction using non-coupled binding energies of intermediates as descriptors of catalytic activity. In contrast to CO₂ electroreduction that can proceed via multiple multielectron reduction pathways (from 2e⁻ reduction to CO or formate to 12e⁻ reduction to ethanol, and beyond), EC is consistently a 2e⁻ reduction, which somewhat simplifies the process modeling. On the other hand, predicting the outcome of EC is more complicated due to a large scope of potential organic substrates that can be carboxylated, although they can be regarded more generally as specific functional groups with the effects of substituents quantifiable via their electron donating or withdrawing nature. Another major complication for the theoretical prediction of electrocatalyst performance in EC is a lack of reliable

heterogeneous DFT models for describing radical anions and electron transfer in an aprotic media, and developments on this front will be instrumental for accelerating catalyst discovery in this field. Attempts to generate volcano plots (Sabatier principle) have been made for the electroreduction of organohalides in aprotic medium where activity was plotted as a function of the bonding energies between the metal and a halide ion, which only vaguely complied with a volcano relationship.⁸¹ Exploring the binding affinity of the key reaction intermediates to the electrode surface is a more promising and underexplored route to evaluating activity trends in electroreductive organic transformations. However, it is important to understand that only simple reactions follow Sabatier principle with just one descriptor, while more complex reactions that can give multiple products may follow more complex selectivity trends.

Due to a clear map of how various single-component materials perform in CO₂ electroreduction, this field has moved to screening various exposed electrocatalytic surfaces and multicomponent systems and interfaces. It has also been established that specific atomic arrangement on the electrode surface can favor the stabilization of certain reaction intermediates, thereby allowing to guide reaction selectivity not only by selecting the electrode composition, but also by carefully designing its nanoscale morphology (Figure 1.10b).¹¹² In addition, various surface defects such as ad-atoms, grain boundaries, subsurface oxide species, as well as the local environment in the vicinity of the electrode surface were shown to affect the reaction course (Figure 1.9c).^[69] Furthermore, nanoscale structural effects beyond the atomic arrangement have also been shown to be important factors affecting both activity and selectivity of CO₂ electroreduction: field-induced reagent concentration by nano-features with high curvature was shown to promote CO₂ electroreduction.¹¹³ Meanwhile, even the empirical knowledge of the effects of the electrode atomic and nanoscale structure on the adsorption and stabilization of key reaction intermediates in EC remains in a relatively preliminary stage. The complexity of these studies lies in the variety of possible atomic and nanoscale electrocatalyst surface configurations responsible for the formation of a particular product. However, developing a systematic understanding of these effects in heterogeneous electrocatalysts on the outcome of an EC reaction targeting a particular high-value product will immensely expedite the process optimization. The more is understood in terms of catalytic trends for a specific EC product or product class, the easier it will become to arrive to such an understanding for a different target product. Electrolyte effects are now being systematically studied in CO₂ electroreduction by implementing a combination of

DFT and MD simulations in addition to experiments: it is unclear how the observed trends and methods can be translated to EC, however the electrolytes are known to have a significant effect on the course of EC, so it is certainly essential to include these considerations for full system modeling and accurate predictions. To understand the trends in the performance of electrocatalysts in EC more broadly, a large parameter space of organic substrate with a strong effect of substituents, along with the effect of other reaction parameters (including the electrode voltage) needs to be considered, which implies many iterations of experimental and theoretical studies. Recent advancements in applying machine learning algorithms for refining CO₂ electroreduction

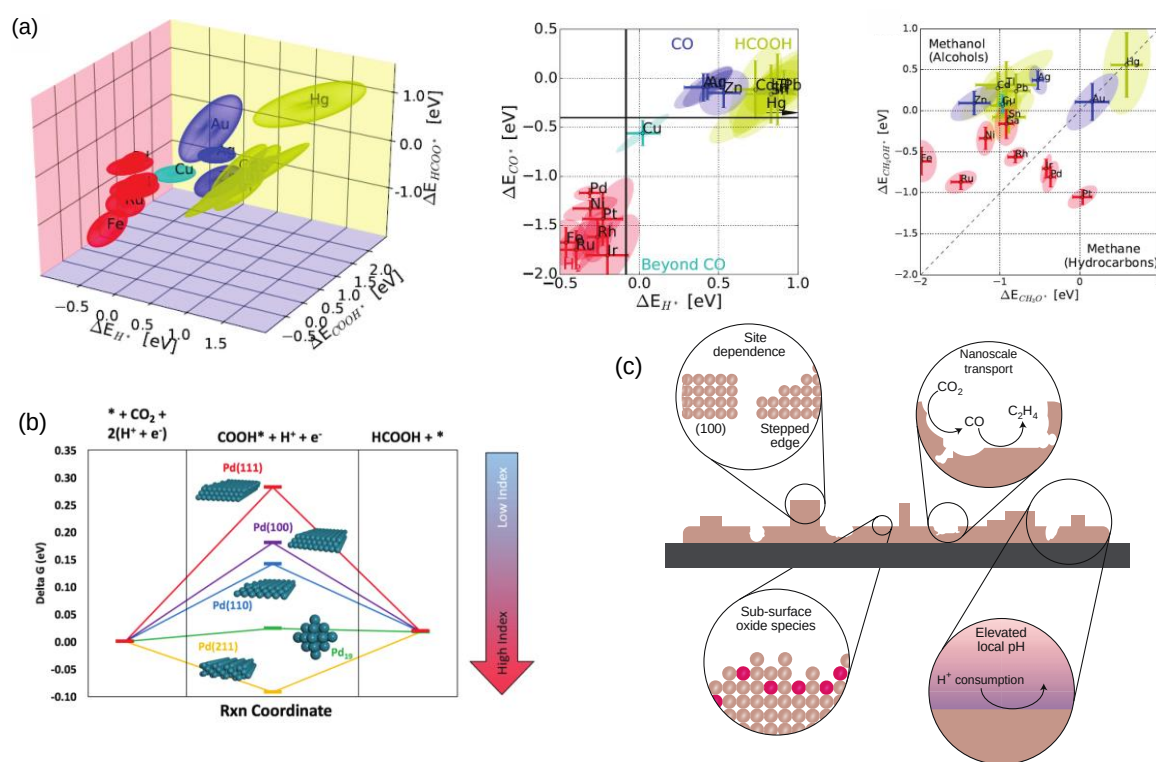


Figure 1. 10: Catalyst optimization strategies in CO₂ electroreduction. (a) Mapped performance of single metals using binding energies of key reaction intermediates as descriptors of CO₂ electroreduction towards various products;¹¹⁵ reproduced with permission from ref. [115], Copyright 2017, Wiley-VCH. (b) Free energy diagrams for the electrochemical reduction of CO₂ to formate on different Pd facets;¹¹² reproduced with permission from ref. [112], Copyright 2016, American Chemical Society. (c) Motifs on a metal electrode surface that may influence C-C bond formation in CO₂ electroreduction.⁶⁹ Reproduced with permission from ref [69]. Copyright 2019, Springer Nature.

catalytic parameter space in a high-throughput way¹¹⁴ could be adapted in the future to accelerate catalyst and reaction optimization in the EC parameter space.

In terms of building an experimental body of data for understanding electroorganic reaction trends and developing new electrosynthetic methodologies, the lack of standard cells and protocols for conducting electroorganic synthesis on laboratory scale and consequent effects on the reproducibility of the results has been widely commented on.^{116,117} Currently a lot of efforts are directed to the development and adaptation of universal batch and flow cells for electroorganic synthesis,^[116,118,119] but problems still remain and reaction involving gasses are overlooked in the proposed solutions. At the same time, significant advances have been made in recent years in the development of practical CO₂ electrolyzers based on three-phase interface architecture integration (gas CO₂ - liquid/polymer electrolyte - solid electrocatalyst) and understanding of the multiscale effects occurring in this system (Figure 1.11a).¹²⁰ While this system is indispensable for overcoming intrinsic limitations of electrolysis involving CO₂ (solubility limits, mass transport limitations), a direct adaptation of these gas diffusion electrode (GDE)-based devices to EC reactions is not feasible as aqueous CO₂ electroreduction GDEs rely on hydrophobic layers, which are generally incompatible with organic electrolytes required for EC. However, non-aqueous GDE have been recently developed for nitrogen electroreduction in non-aqueous media,¹²¹ which may well be transferable to EC systems (Figure 1.11b). Considering industrial potential of EC reactions, it is reasonable to not only study the electrocatalyst performance using standardized equipment, but also benchmark their performance at commercially viable combinations of potentials and current densities.¹²² Thus, GDE-based reactors hold promise for EC, along with other novel technical solutions that can be inspired by the interface and similarities between these different electroreductive catalytic technologies involving gases as reagents.

Another research sub-direction in CO₂ electroreduction that has gained increasing attention recently is related to the development and optimization of techno-economic analysis and life cycle analysis approaches to evaluate the feasibility and impact of industrial implementation of a specific CO₂ electroreduction solution.¹²³⁻¹²⁵ Even with further maturing of this technology, its commercialization still requires that the products synthesized via CO₂ electroreduction must be economically competitive with the market prices for equivalent fuels or chemicals produced through traditional methods.

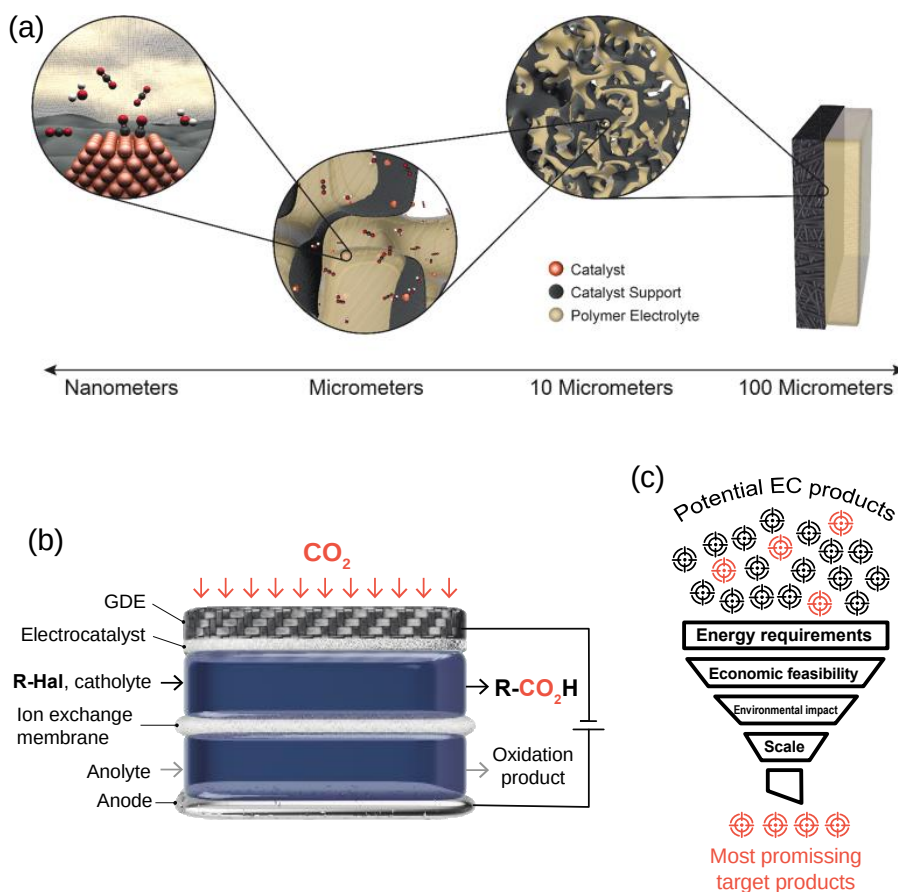


Figure 1. 11: Systems approach to EC optimization. (a) Schematic of a three-dimensional GDE depicting the multiscale phenomena occurring during CO_2 electroreduction;¹²⁰ reproduced with permission from ref. [120], copyright 2019, American Chemical Society. (b) Conceptual design of a GDE-based EC electrolyzer. (c) Conceptual approach to identifying the best EC targets using TEA and LCA.

The same competitiveness requirement applies to the sustainability metrics, which can be determined in LCA. In addition, early-stage techno-economic analysis and life cycle analysis can also be used to compare the industrial viability of various specific CO_2 electroreduction solutions, considering the combined effect of the catalyst, electrolyte, cell configuration, and all reaction parameters, therefore allowing for a feedback loop informed by the assessment model and a targeted optimization of specific metrics. When it comes to EC, it is important to recognize that although the electrochemical approach in general is a sustainable and powerful platform for organic synthesis, this does not imply that any electroorganic reaction is more environmentally friendly compared to traditional methods.¹²⁶ It is therefore important to identify and develop EC

routes that specifically deal with challenges that cannot be solved by traditional methods, as well as to minimize, recycle or completely avoid the use of supporting electrolytes. Thus, an early-stage techno-economic analysis and life cycle analysis of specific EC methods can advise which metrics need to be further improved and to what extent, and how to prioritize further development. Due to a huge scope of organic precursors and, therefore, potential EC products, there is an added layer of complexity as a target product needs to be identified from a large pool of possibilities. Certainly, developing such assessment frameworks is difficult, however, the existing CO₂ electroreduction techno-economic analysis and life cycle analysis models can serve as reference points thus providing a head start for establishing an early-stage EC assessment methodology.^{127,128}

As electrolysis is an intrinsically coupled reaction by the virtue of requiring an anodic and a cathodic process, systems design should consider this in greater detail as it can be used to improve the reaction atom economy, technoeconomics, and sustainability of the overall process. Indeed, an integration of CO₂ electroreduction with different anodic reactions has gained increasing attention, focusing on treating waste on the anode,¹²⁹ and many of these processes can be compatible with EC.^{76,109} In addition to borrowing anodic co-reactions from CO₂ electroreduction, EC can benefit from the developments in the electroorganic anodic reactions that have been studied more widely than cathodic reactions.¹⁷ Moreover, a techno-economic analysis framework for electrochemical coproduction via coupling CO₂ electroreduction with a value-added organic oxidation was recently reported, concluding that this paired approach can secure significant economic feasibility.¹³⁰

1.8 Scope of this thesis

This thesis presents the comprehensive study of a sacrificial-anode free EC in divided systems focusing on the electrocatalyst and cell design, anodic reaction screening, as well as overall EC conditions optimization. Chapter 2 includes the description of experimental methods for nanoparticle synthesis, material characterization, electrochemical experiments, and product analysis used in this thesis. Chapter 3 explores EC in divided systems including reaction optimization in H-type electrochemical cell (membrane choice, effect of applied potential, precursor concentration, as well as overall reaction conditions) followed by the EC mechanism elucidation for sacrificial-anode free systems, and anodic reactions screening. Chapter 4 explores the electrocatalytic activity of bulk metals and carbon materials for EC in divided systems. Chapter 5 explores the synthesis of Cu, Au, and Pd nanoparticles (NPs) as catalysts for EC, as well as the effect of NP composition, surface chemistry, and morphology on the EC outcome followed by the study of the NP stability under EC conditions using scanning electron microscopy (SEM). Chapter 6 explores pressurized electrochemical cell capabilities in EC at high concentrations of benzylic bromides and presents 2D map of the carboxylate FE dependence on the CO₂ pressure. Chapter 7 provides the conclusions of the presented in this thesis work as well as future works.

Chapter 2 Materials and methods

2.1 Materials

Cetyltrimethylammonium bromide (CTAB, $\geq 99.0\%$, BioUltra, for molecular biology), cetylpyridinium chloride (CPC, USP grade), hydrochloric acid (HCl, 37%, ACS reagent), palladium(II) chloride (PdCl_2 , 99.9%), L-ascorbic acid (AA, $\geq 99\%$, anhydrous, ACS grade), sodium L-ascorbate (SLA, $\geq 98\%$), copper (II) acetate hydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\geq 98\%$, ACS reagent), copper (II) nitrate dihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99–104% (RT)), copper (II) chloride CuCl_2 (99.999%), copper(II) sulfate (CuSO_4 , $\geq 99.99\%$), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$, used for the synthesis of Au BNPs), sodium borohydride (NaBH_4 , $\geq 98.0\%$), gold(III) chloride solution (HAuCl_4 , 99.99%, 30 wt.% solution in dilute HCl), hydrogen peroxide (H_2O_2 , 30 wt.% solution in H_2O), sodium hydroxide (NaOH , $\geq 97\%$, ACS grade), Ag foil ($> 99.9\%$), Pt foil ($> 99.9\%$), acetonitrile (CH_3CN , ACN, MeCN; anhydrous, 99.8%), N-benzylideneaniline (99%), benzyl bromide (98%), benzyl chloride (99%), 4-methylbenzyl bromide (97%), (1-bromoethyl)benzene (97%), sodium iodide ($> 99\%$), 4-(bromomethyl)benzonitrile (99%), bromodiphenylmethane (95%), bromotriphenylmethane (98%), tetrabutylammonium iodide (TBAI, $\text{C}_{16}\text{H}_{36}\text{IN}$, $\geq 99.0\%$), and potassium bicarbonate (KHCO_3 , 99.5–101.0%) were purchased from SigmaAldrich. Cetyltrimethylammonium chloride (CTAC, $> 95\%$) and tetrabutylammonium bromide (TBABr, $\text{C}_{16}\text{H}_{36}\text{BrN}$, $> 98\%$) were purchased from TCI. Gold foil (99.95%, thickness 0.05mm), palladium foil (99.9%, thickness 0.025mm), tetraethylammonium tetrafluoroborate (TEABF_4 ; 99%), sodium salicylate (NaSal , 99%), and Brij L23 (Brij 35, Tricosaethylene glycol mono-n-dodecyl ether) were purchased from Alfa Aesar. Cu, Ni, Ti, Zn, Fe, Al, Sn, and Pb foils ($> 99\%$) were purchased from VWR. Silver nitrate (AgNO_3 , 99.98%) was purchased from Engelhard Industries. Ar (99.998%) and CO_2 (99.999%) was purchased from Praxair. Toray carbon paper (060, Wet Proofed) was purchased from FuelCellStore. All chemicals were used as received without further purification. All solutions were freshly prepared before use. Ultrapure water (Millipore, $18.2 \text{ M}\Omega \text{ cm}$) was used for all aqueous solutions. The solutions of organic electrolytes were kept over molecular sieves prior to use.

2.2 Methods

2.2.1 Nanoparticle synthesis

2.2.1.1 Synthesis of Pd cubic seeds

The synthesis of Pd cubic seeds was previously reported elsewhere.¹³¹ Briefly, 45.6 mg of CTAB were dissolved in 10 mL of Milli-Q water in a 20 mL vial that then was placed in an oil bath at 95 °C and stirred for 10 minutes. Then 250 μ L of 20 mM H_2PdCl_4 solution was added, and the reaction mixture was stirred for 5 minutes, followed by the addition of 200 μ L of 0.1 M AA solution. After 10 minutes of stirring at 800 rpm the solution was transferred into a 30 °C bath without stirring for 1 hour to age. The resulting solution was distributed in 10 centrifuge tubes, 1 mL in each, washed using 2 centrifugation cycles, at 14 000 g for 14 min and at 11 000 g for 11 min, and each tube was topped up with 1 mL of 15 mM CTAC solution to make the final stock solution.

2.2.1.2 Synthesis of raspberry-like (RL) Pd-seeded Cu NPs

86.4 mg of CTAC was dissolved in 18.5 mL of Milli-Q water in a 20 mL vial, then 170 μ L of 0.1 M $\text{Cu}(\text{OAc})_2$ solution was added in one shot. After that, 300 μ L of 0.5 M SLA solution was added in one shot followed by a light shaking of the vial. Finally, 1 mL of Pd seeds stock solution was added, and the resulting light-brown mixture was placed in a 110 °C oil bath for 25 minutes. Colour changed to red within 5 minutes. The reaction was quenched in an ice bath, concentrated, and washed with 2 centrifugation cycles at 5000 g for 5 minutes. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.3 Synthesis of cage Pd-seeded Cu NPs

57.6 mg of CTAC was dissolved in 12.35 mL of Milli-Q water in the 20 mL vial, then 113 μ L of 0.1 M $\text{Cu}(\text{OAc})_2$ solution was added in one shot, followed by the addition of 200 μ L of 0.5 M SLA solution. Lastly, 1 mL of Pd seeds stock solution was added, and the reaction mixture was mixed well by swirling the vial, which was then placed in a 110 °C oil bath for 25 minutes so that only a half of the vial was immersed in the oil bath. The reaction was quenched in an ice bath,

concentrated and washed using 2 centrifugation cycles at 5000 g for 5 minutes. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.4 Synthesis of CPC-capped Au spherical NPs (NSs)

The synthesis of Au CPC-capped NPs was previously reported elsewhere.¹³² (i) 3 nm Au nanoparticles were synthesized by the addition of 0.6 mL of ice-cold 10 mM NaBH₄ solution into the vigorously stirred mixture of 0.167 mL of 15 mM HAuCl₄ and 10 mL of aqueous 0.1 M CTAB. After two hours of aging, seed solution was diluted to 100 mL; (ii) 0.6 mL of this solution was added into the diluted to 50 mL mixture of 4 mL of 0.24 M CTAB, 0.133 mL of 15 mM HAuCl₄, and 3 mL of 0.1 M AA under mild stirring. Resultant was left to react overnight undisturbed. As prepared Au octahedrons were washed once water at 16000 g and redispersed in 50 mL of water. (iii) All volume of Au octahedrons was placed in 500 mL Erlenmeyer flask and diluted to 200 mL. Then 32 mL of 0.1 M CPC solution was added, heated in 30 °C water bath for 5 minutes under mild stirring. Then the solution was removed from the water bath, 5 mL of 15 mM HAuCl₄ solution was added, followed by 16 mL of 0.1 M solution of AA. Resultant was left undisturbed for 8 hours. (iv) Formed in (iii) NPs were washed for 15 min at 27 °C at 5000 g and redispersed in the same volume. Then, the resulting solution was mixed with 0.1 M FeCl₃ solution in 1:1 volume ratio and left for 2 hours under occasional stirring. The etched Au spherical NPs were washed for 15 min at 5000 g, topped up with 50 mM CPC, washed with water again, and concentrated. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.5 Synthesis of Au citrate NPs

Au citrate NPs were synthesized using procedure reported elsewhere.¹³³ 20.9 mg of HAuCl₄·3H₂O was dissolved in 180 mL of water. Resulting solution was placed in an Erlenmeyer flask, covered with aluminium foil, and placed on a preheated to 240 °C stirring plate with 300 rpm stirring. When the solution started boiling, 18 mL of 1%wt sodium citrate solution was added in one shot. After 5 minutes formed NP solution was left to cool down to room temperature and concentrated *via* centrifugation at 1500 g for 25 minutes 3 times. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.6 Synthesis of Au BNPs

Au BNPs were prepared according to the previously reported procedure.¹³⁴ First, Au seeds were synthesised by the addition of the 1 mL ice-cold 100 mM NaBH₄ into the mixture of 1 mL of 10 mM HAuCl₄, 1 mL of 10 mM sodium citrate, and 36 mL of water under mild stirring. The resulting mixture was left undisturbed for 3 hours. Au BNP growth was performed in two steps. First, 0.1 mL of Au seeds were added to the aqueous mixture of 1 mL of 0.2 M Brij L23, 1 mL of 0.1 M CTAB, 0.08 mL of 10 mM HAuCl₄, 0.01 mL of 5 mM AgNO₃, 0.2 mL of NaSal, and 0.02 mL of 0.1 M AA. Second, 0.1 mL of the solution that was prepared on the first step was added to the mixture of 10 mL of 0.2 M Brij L23, 10 mL of 0.1 M CTAB, 0.8 mL of 10 mM HAuCl₄, 0.1 mL of 5 mM AgNO₃, 2 mL of NaSal, and 0.2 mL of 0.1 M AA. Resultant was vigorously shaken for 1 min, left undisturbed for 8 h, washed using centrifugation cycle at 3000 g, and concentrated. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.7 Synthesis of Au core-cage (CCs) NPs

The synthesis of Au-Au CCs was previously reported by our group elsewhere.¹³⁵ Briefly, (i) 3 nm Au nanoparticles were synthesized by the addition of 0.6 mL of ice-cold 10 mM NaBH₄ solution into the vigorously stirred mixture of 0.167 mL of 15 mM HAuCl₄ and 10 mL of aqueous 0.1 M CTAB. After two hours of aging, seed solution was diluted to 50 mL; 6 mL of this solution was added into the diluted to 1 L mixture of 100 mL of 0.2 M CTAB, 2.66 mL of 15 mM HAuCl₄, and 50 mL of 0.12 M AA under mild stirring. Resultant was left to react overnight undisturbed. As prepared Au octahedrons were concentrated to 5 mL, washed twice with water, and redispersed in 5 mL of water. (ii) Au@Ag core-shell NPs were synthesized by the consequent addition of 1 mL of 10 mM AgNO₃ and 4 mL of 1 M AA into the preheated to 60°C mixture of 2.5 mL of concentrated Au octahedrons and 5 mL of 0.3 M aqueous CPC solution. Reaction was left to proceed under intense stirring on the thermomixer for 1 h, then cooled down, washed once, and redispersed in 62.5 mL of water. (iii) 0.1 mL of 1 mM HAuCl₄ was added dropwise into 1 mL of the Au@Ag cubes at a rate of 2 mL min⁻¹ under vigorous stirring on thermomixer, followed by the addition of 0.05 mL of H₂O₂. Resultant – Au-Au CCs – were washed once at a high speed, once at a low speed, concentrated, and used as prepared for imaging and electrode preparation.

2.2.1.8 Synthesis of Pd NCs

Pd NCs were synthesized following a procedure reported elsewhere.¹³¹ For Pd nanocube synthesis, a solution of 36.5 mg of CTAB in 8 mL of H₂O was heated to 95 °C under stirring, followed by the addition of 0.2 mL of 20 mM H₂PdCl₄ solution and 0.16 mL of 0.1 M ascorbic acid. After 10 min of stirring the reaction mixture was cooled down and aged for 1 h. Separately, 1.6 mL of 100 mM H₂PdCl₄ was added to the solution containing 0.5 g of CTAB and 5 mL of H₂O under stirring at 45 °C followed by the addition of 5 mL of Pd nanocubes synthesised on the first step and 1.25 mL of 1 M ascorbic acid. The resulting mixture was vigorously stirred at 45 °C for 6 h. The synthesized Pd NCs were centrifuged once at 4000 g and twice at 3500 g for 10 minutes at 27 °C. The resulting concentrated solution was further used for imaging and electrode preparation.

2.2.1.9 Synthesis of Pd BNPs

The synthesis was performed according to the procedure reported elsewhere.¹³¹ Firstly, Pd polygonal seeds were synthesised. 345 mg of CTAB was dissolved in 10 mL of 0.25 mM solution of Na₂PdCl₄ in a 50 mL two-neck round-bottom flask, the solution was bubbled with Ar for 30 minutes under stirring at 30 °C, followed by the injection of 0.22 mL of 15 mM ice-cold NaBH₄ aqueous solution. Then 0.168 mL of this solution was added to the mixture of 690 mg CTAB, 20 mL of 0.25 mM Na₂PdCl₄, and 0.156 mL of 0.1 M AA. Resultant was shaken for 1 minute and left undisturbed for 2 h. Secondly, seed-mediated growth of branched Pd nanoparticles was performed. 1 g of CTAB was dissolved in 6.8 mL of water and stirred at 30 °C, then 1 mL of 100 mM CuSO₄ was added, followed by the consequent addition of 3.2 mL of a solution containing 100 mM of Na₂PdCl₄ and 0.25 M of HCl, and 10 mL of the polygonal seeds, and 5 mL of 1 M AA. Resulting mixture was stirred for 24 hours at 45 °C, washed 2 times, concentrated, and then used for the imaging and electrode preparation.

2.2.2 Material characterization

2.2.2.1 SEM, TEM, and EDX

Samples for scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX) were prepared by placing the drops of

the purified colloidal solution of NPs onto a stainless-steel plate, Cu grid, and Ni grid, respectively. Samples for NP electrochemical stability studies were prepared by attaching the piece of electrode electrode (foil with deposited particles) to the stainless-steel plate using conductive tape (NEM tape, Nisshin EM). SEM and TEM were performed using Hitachi S5200 microscope operating at 30 kV. EDX was performed using Hitachi HF3300.

2.2.2.2 XPS

The surface analysis of the electrodes comprised of metal nanoparticles with different shapes was performed using X-ray photoelectron spectroscopy with an Thermo Fisher Scientific K-Alpha system.

2.2.2.3 XRD

Samples for XRD were prepared by drying washed and concentrated colloidal solutions of NPs under Ar. XRD was performed using Bruker D8Advance powder X-ray diffractometer.

2.2.2.4 Raman spectroscopy

Samples for Raman spectroscopy were prepared by depositing metal NPs on cleaned and polished Ti foil and attached to a glass slide. Raman spectroscopy was performed using Renishaw inVia Reflex Raman microscope. Measurements were performed using a 532 nm laser (Renishaw DPSSL, 50 mW) at 10% power.

2.2.2.5 UV-visible spectroscopy

UV-visible spectra were acquired using Ocean Optics DH-2000-BAL lamp and Ocean Optics Flame-S-XR1-ES detector in a 1 cm quartz cuvette.

2.2.3 Electrode fabrication

2.2.3.1 Preparation of bulk electrodes

12 polycrystalline bulk metals were screened as cathodes in this work: Ag, Au, Pt, Pd, Cu, Ni, Ti, Zn, Fe, Al, Sn, and Pb. Apart from Ag, Au, Pt, Pd, and Ti foils, all metal surfaces were mechanically cleaned to remove oxide layer and then sequentially polished with 0.3 μm and

50 nm alumina powders prior to electrochemical measurements. After polishing, the electrodes were washed with Milli-Q water in an ultrasonic bath and then rinsed with acetonitrile. The cleaning procedure was repeated prior to each measurement to minimize the effect of surface oxides on the electrochemical performance of the cathodes. The carbon-based cathode materials (glassy carbon (SPI Supplies), carbon cloth (AvCarb 1071 HCB, FuelCellStore), and carbon paper (Toray Carbon Paper 060, Wet Proofed, FuelCellStore) were used as received. The surfaces of all the studied materials after the cleaning were characterized by scanning electron microscopy, illustrating that their surface morphologies were comparable on the nanoscale. In addition, the double layer capacitance of all electrodes was measured.

2.2.3.2 Preparation of nanostructured cathodes

The inks for electrode preparation were made of concentrated aqueous solutions of NPs. Ink concentrations were set to 10 mg mL⁻¹. 25 μ L of that ink was deposited on 0.5 x 0.5 cm substrate (polished Ti foil or Toray carbon paper). Cu-based electrodes were dried and stored under Ar to prevent oxidation. Au CC electrodes were washed with methanol, soaked in 0.1 M ammonia solution for 30 minutes, and rinsed in water. Resulting electrodes were used as is or washed with methanol and water.

2.2.4 Electrochemical experiments

2.2.4.1 Electrochemical cell assembly

All electrochemical reactions in this work were performed in a two-compartment cell, equipped with an ion exchange membrane (Nafion 117, Fumasep FBM-PK or Fumasep FAB-PK-130, FuelCellStore), using metal foils or nanostructured electrodes as cathodes, graphite rod or Ni-foam supported Ni hydroxides as anode, and Ag-wire quasi-reference electrode for organic medium or Ag/AgCl reference electrode for aqueous medium and connected to an electrochemical workstation (Biologic SP-300). All potentials in organic medium are reported vs. Ag-wire (Ag/Ag⁺; quasi-reference electrode was also calibrated with Fc/Fc⁺ redox couple).

2.2.4.2 Pb UPD

The lead underpotential deposition was performed according to the procedure reported elsewhere.¹³⁶ Briefly, lead UPD was conducted by cyclic voltammetry in the argon-saturated solution of 0.1 M NaOH containing 1 mM Pb(NO₃)₂ over a potential range of −0.7 V to −0.2 V (versus Ag/AgCl) at a scan rate of 50 mV s^{−1}.

2.2.4.3 Cyclic voltammetry (CV)

CV experiments were carried out in a three electrode H-cell equipped with an AEM (Fumasep FAB-PK-130, FuelCellStore), Pt-mesh, Ni foam, or graphite rod anode, and Ag wire quasi-reference electrode. A solution of 0.1 M TEABF₄ in CH₃CN was used as an electrolyte for both cathodic and anodic compartments. For coupled experiments 5 M or 1 M KOH was used as anolyte. For selected experiments 0.1 M TBABr in CH₃CN was used as catholyte. Before each experiment the catholyte was saturated with Ar or CO₂ by continuously delivering the gas at a rate of 10 mL min^{−1} for 15 min, and the solution headspace kept under a positive pressure of a corresponding gas (Ar or CO₂) during the electrochemical measurements to eliminate the presence of oxygen. All CVs were recorded within the electrolyte and electrode stability windows to avoid the effects of the electrolyte decomposition or metal oxidation on the CV behavior.

2.2.4.4 Potentiostatic electrolysis (CA)

CAs were performed in the same electrochemical cell as described above; For EC reaction CO₂ was continuously bubbled through the reaction mixture at the rate of 14 mL min^{−1}. Reactions were stopped after passing 1 F mol^{−1}, unless otherwise stated. The identification of reaction products was carried out by gas chromatography and nuclear magnetic resonance (NMR). Liquid products were analyzed by ¹H NMR of crude reaction mixtures combined with an internal standard (1,2,4,5-tetrachlorobenzene) and compared against the previously reported NMR data for R-CO₂R, and R-R.

2.2.4.5 CV and CA in a pressurized cell

EC experiments under elevated CO₂ pressure were performed using in-house made 3-electrode H-cell manufactured from PEEK and equipped with AEM (Fumasep FAB-PK-130, FuelCellStore). Cu-based electrode was used as a cathode, graphite was used as an anode, and Ag

wire quazi-reference electrode was used as a reference electrode. Electrochemical reactions were performed similarly to these in non-pressurized cell except for the gas delivery. In the pressurized cell Ar or CO₂ was delivered in a sealed compartment until certain pressure was reached. Then, given pressure was kept for 30 minutes before a valve to a gas tank was closed.

2.2.5 Synthesis of organic compounds

2.2.5.1 Synthesis of benzyl iodide

Sodium iodide (4.5 g) was dissolved in 20 mL of acetone at 0 °C. Benzyl bromide (1.8 mL) was slowly added to the reaction mixture and the reaction was left to stir overnight at the room temperature in the dark. On the next day, 40 mL of brine was added to the reaction mixture and obtained solution was extracted with diethyl ether (3 x 25 mL). The extracts were dried over MgSO₄ and concentrated under reduced pressure. The crude mixture was filtered through silicagel (20 mL SiO₂; eluent: petroleum ether –Et₂O 95:5) to give benzyl iodide as a brown liquid (2.9 g, 91%). ¹H NMR (300 MHz, CDCl₃) δ, ppm, 4.45 (CH₂), 7.22-7.26 (m, 3H), 7.28-7.38 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ, ppm, 139.3, 128.8, 128.7, 127.9, 5.7.

2.2.6 Product analysis

2.2.6.1 In-line analysis of gaseous products with GC

Faradaic efficiency measurements of the gas products were performed using Agilent 7890B GC System, equipped with the sequence of multiple columns for efficient separation of gas products (H₂, CO, CH₄, C₂H₄), and bypassing CO₂. Gaseous products were analyzed using in-line gas chromatography (GC) analysis every 20 minutes until the completion of the reaction. The quantitative analysis of the gas products was performed using a thermal conductivity detector (TCD) and a flame ionization detector (FID). The FE of the gas products was calculated as

$$FE(\%) = n_i F \Phi_i F_m / I,$$

where n_i is a number of the electrons transferred, F is the Faraday constant, Φ_i is a volume fraction of the gas product being quantified (calculated by calibrating the GC data using a diluted mixture of gases of known concentrations), I is a current value at the beginning of the measurement, F_m is the molar CO₂ gas flow rate.

2.2.6.2 Analysis of liquid products with NMR

Faradaic efficiency measurements of the liquid products of EC were performed using ^1H NMR on Bruker 300 MHz NMR spectrometer. In a typical experiment, 0.8 mL of reaction mixture was evaporated, the residue was dissolved in 0.8 mL of CDCl_3 with 1,2,4,5-tetrachlorobenzene additive (108 mg in 15 mL of CDCl_3) that was used as an internal standard.

Procedure for quantification: After the electrolysis, 0.7 mL of the catholyte was taken as a sample, then the solvent was evaporated to obtain a colorless or bright yellow oil (with the presence of colorless crystals). This mixture was dissolved in 0.8 mL of 33.3 mM solution of 1,2,4,5-tetrachlorobenzene in CDCl_3 and analyzed using Bruker 300 MHz NMR spectrometer. For every sample 64 scans were recorded. Peak areas of products were compared to the peak area of the standard (2H singlet at 7.55 ppm).

Since NMR signals are shifted from the standard values due to the electrolyte present in the mixture, ^1H -NMR of reaction mixtures without the electrolyte were also analyzed and compared with the literature data.

Procedure for removing the electrolyte (A): The solvent (ACN) was removed from the reaction mixture after the electrolysis followed by the addition of diethyl ether. We found that all organic products are soluble in Et_2O while the TBAI/TBABr electrolyte is completely insoluble.

Procedure for removing the electrolyte (B): After the electrolysis, the solvent was evaporated under a reduced pressure and the residual material was acidified with 3 mL of concentrated HCl, after 10 minutes additional 3 mL of water was added followed by the extraction of the products with diethyl ether (3x20 mL). The extracts were washed with water and dried over anhydrous MgSO_4 .

After the evaporation of diethyl ether from the solution obtained by method A or B, the residue was analyzed by with ^1H -NMR with the internal standard.

2.2.6.3 Product distribution error estimates

Error bars included in this thesis were determined by repeating an experiment at least 3 times keeping all conditions the same. Any errors associated with the chosen quantification method (e.g., GC, NMR) were not additionally accounted for.

2.2.7 Thermodynamic and kinetic calculations

2.2.7.1 Electrocarboxylation and homocoupling reaction kinetics calculation

Pseudo-first order kinetic conditions are assumed to apply for electrocarboxylation and electrochemical homocoupling for organic halides. The decay in R-Br concentration in the course of electrolysis was calculated based on the first order reaction rate law with the corresponding R-Br concentration dependence on time:

$$C_{R-Br} = C_0 e^{-kt}$$

If the reduction of R-Br is a two-electron process, i.e., $R-Br + 2e^- = R^{2-}$, $Q(t)$ dependence can be calculated as:

$$Q = nF(C_0 - C_{R-Br}) = 2FC_0(1 - e^{-kt}),$$

where n – number of electrons transferred, F – Faraday constant, C_0 – initial concentration of R-Br, C_{R-Br} – concentration of R-Br in the system at moment t_i , k – rate constant, t – electrolysis time. If the reduction of R-Br is a one electron process, i.e., $R-Br + 1e^- = R^{\cdot-}$, $Q(t)$ dependence can be calculated as:

$$Q = nF(C_0 - C_{R-Br}) = FC_0(1 - e^{-kt})$$

The pseudo-first order rate constant k was calculated from the experimental data (Q_i , t_i), where no electrode passivation was detected, and the kinetics of R-Br reduction was the same for all three membranes ($t_i < 1h$).

2.2.7.1 Calculation of Gibbs free energies and cell potentials of electrochemical reactions

To identify energy-saving alternatives to the OER, standard Gibbs free energies of selected coupled reactions (ΔG^0 reaction) and their corresponding standard cell potentials (E^0 cell) have been calculated (equations 1 and 2). Gibbs free energy of formation (ΔG_f^0) values for products and reactants were taken from the literature data or estimated by the Joback method. This method allows to predict pure-component properties from group-contributions. ΔG_f^0 values for glycolic acid, (bromomethyl)benzene and 2-phenylacetic acid were estimated by the Joback method using a designated online software.

$$E_{cell}^0 = \frac{-\Delta G_{reaction}^0}{nF},$$

where E°_{cell} – standard cell potential, ΔG° reaction– standard-state free energy of reaction, n – number of electrons transferred, F – Faraday constant;

$$\Delta G^{\circ}_{\text{reaction}} = \sum v_{\text{product}} \times \Delta G^{\circ}_{f,\text{product}} - \sum v_{\text{reactant}} \times \Delta G^{\circ}_{f,\text{reactant}},$$

where v is the stoichiometric coefficient and ΔG°_f is the Gibbs free energy of formation. For each anodic process, only one product of oxidation was considered: oxygen for water oxidation, acetic acid for ethanol oxidation, glycolic acid for ethylene glycol oxidation, formic acid for glycerol oxidation, gluconic acid for glucose oxidation, nitrogen and carbon dioxide for urea oxidation reaction (UOR), and nitrogen for ammonia oxidation reaction (AOR).

Chapter 3 Electrocarboxylation in divided systems

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Contribution: performed investigation and formal analysis.

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Contribution: performed investigation and formal analysis, assisted with thermodynamic calculations and manuscript writing.

3.1 Introduction

The electrocarboxylation of organic halides ($R-X$) is a green alternative for the synthesis of nonsteroidal anti-inflammatory drugs, such as ibuprofen,¹³⁷ and important precursors in industrial processes, such as cyanoacetic acid, an,^{138,139} and many others.^{140,141} It has been shown that EC of organohalides with different cathodes (e.g., Ag, Cu, and Ni)¹⁴⁰⁻¹⁴³ in undivided cells with sacrificial Mg or Al anodes generally results in the formation of corresponding carboxylic acids with moderate to high yields in the form of magnesium (or aluminum) salts.¹⁴⁴⁻¹⁴⁹ Although the formation of these salts simplifies the work-up procedure, it negatively affects the reaction atom economy due to the anode consumption in the course of reaction. The formation of insoluble products in EC reactions also causes electrode passivation, resulting in large current fluctuations (potentiostatic electrolysis)¹⁵⁰ or drastic increase in the cell voltage (constant current electrolysis).¹⁵¹ In addition, cathode passivation by the formed Mg^{2+} or Al^{3+} insoluble salts hinders the completion of the reaction.¹⁵⁰ From an engineering standpoint, the usage of consumable anodes is impractical and limits the development of EC in flow electrochemical systems. Replacing sacrificial anodes with alternative anodic reactions at nonsacrificial anodes could offer a potential solution to overcome these limitations. While divided cells with nonsacrificial anodes have been reported for EC of several organic substrates,¹⁵²⁻¹⁵⁵ for halides any mentions are limited to unsuccessful attempts.^{156,157}

Despite EC reactions of organic halides with Mg or Al anodes giving high yields of carboxylation products, their exact formation mechanism remains unclear. The electrochemical reduction of $R-X$ in the presence of CO_2 is a three-step process: (1) halide reduction to a radical

$R^\bullet$, (2) $R^\bullet$ reduction to the corresponding anion R^- , and (3) nucleophilic addition of R^- to CO_2 with a formation of carboxylate anion.¹⁵⁸ Mechanistic interpretations in previous works¹⁴⁴⁻¹⁴⁹ operated on the assumption that electrochemically produced Mg^{2+} ions participated in the reaction only by interacting with the carboxylate anion to form a corresponding salt¹⁵⁹ (Figure 3.1, pathway I).

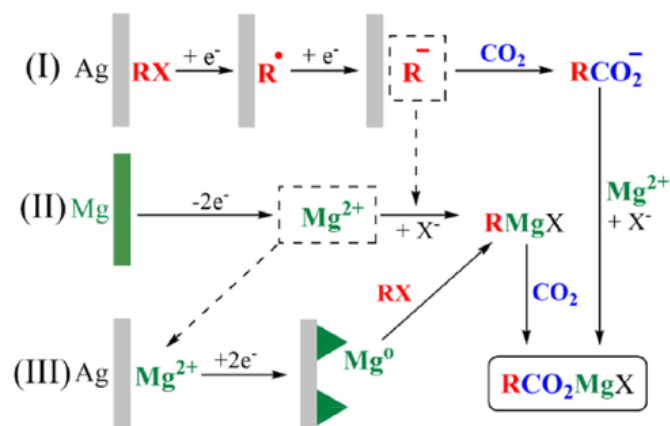


Figure 3. 1: Possible pathways of organic halide carboxylation in undivided electrochemical cells with mg sacrificial anodes. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

However, R^- can also uptake Mg^{2+} ion that selectively reacts with CO_2 , producing a corresponding carboxylate with quantitative yields¹⁶² (Figure 3.1, pathway II). Additionally, the formation of Grignard reagents from organic halides in electrochemical cells with Mg anodes has been observed in the absence of CO_2 .^{160,161} The majority of reported EC of $R-X$ was performed at constant current conditions,¹⁴⁰⁻¹⁴⁹ resulting in inevitable large potential fluctuations.¹⁵¹ Consequently, at high negative potentials, the reduction of Mg^{2+} to Mg^0 [$E^\circ = -2.38$ V vs standard hydrogen electrode (SHE)] at the cathode could facilitate the Grignard reagent formation¹⁶³ (Figure 3.1, pathway III), in addition to enabling competing CO_2 electroreduction.¹⁶⁴ Other sacrificial anodes (e.g., Al and Zn) have similar reactivity: generated Zn^{2+} or Al^{3+} can be cathodically reduced to their metal forms, which, in addition to causing cathode passivation,¹⁵¹ produce organometallic compounds by reacting with organic halides.^{164,165} These organometallic compounds can react with CO_2 , producing corresponding carboxylic acids.¹⁶⁶⁻¹⁶⁹ Thus, the chemistry of $R-X$ reduction in the presence of CO_2 in undivided cells with sacrificial anodes is

rather complex and convoluted, with carboxylate anions potentially originating from the electrochemically assisted Grignard reagent, rather than the direct EC process.

Here we aimed to develop a feasible electrochemical coupled system with cathodic EC and sustainable anodic process in aqueous medium. We established that EC can be efficiently coupled with well known counter reactions such as oxygen evolution reaction (OER) as well as urea and ammonia electrooxidation (UOR and AOR, respectively). The adaptation of the two latter anodic processes is especially beneficial due to their value-added wastewater treatment application as well as the decrease in total cell voltage of an electrolyzer compared to sluggish OER. We investigated the new sacrificial anode-free electrocatalytic system for EC in detail and suggested the optimal operation conditions including membrane type, applied potential, substrate concentration, etc. Based on the extensive experimental results, we proposed a detailed mechanism for major electrochemical products formation supported by density functional theory (DFT) calculations.

3.2 Membrane optimization

Aiming to assess the potential of purely electrochemical fixation of organohalides to CO₂ decoupled from sacrificial anodes, we contemplated performing this reaction in a divided electrochemical cell with a well-established process at the anodic side. Direct CO₂ electrolyzers typically rely on the OER as an anodic process,¹⁶⁹⁻¹⁷¹ although other oxidation reactions are now considered as well to minimize the cell voltage for their commercial implementation.^{169,172} The mechanism of OER and catalysts for this reaction are well-established due to their importance in water splitting for electrochemical hydrogen production.^{173,174} The difficulty of adopting OER for EC lies in poor solubility of organic substrates in aqueous electrolytes and the need of an aprotic environment for the organic substrate to avoid intermediate protonation.^{158,175} We hypothesized that this complication can be overcome by introducing an appropriate membrane that can render the aprotic and aqueous compartment segregation. Cation-exchange membranes (CEMs) have been previously used in EC reactions in fully organic electrolytes to provide counterions for the carboxylate anions generated at the cathode.^{140,152,155} However, released halide ions (Hal⁻) accumulate in the catholyte, causing unwanted side reactions (alkene formation due to the Hal⁻ catalyzed elimination reaction).^{140,176,177} In addition, in the case of an aqueous anolyte and an aprotic catholyte, CEM may enable competing the hydrogen evolution reaction (HER) at the cathode by allowing the passage of protons. An anion-exchange membrane (AEM), whose performance has never been studied in EC reactions, could address these issues; however, with this membrane, counterions for the carboxylate anions can only be provided by the catholyte, resulting in its consumption. A bipolar membrane (BPM), which consists of anion and cation exchange layers, combines the properties of both and potentially may either solve or exacerbate the problems associated with CEM and AEM.

A divided electrochemical cell with two compartments separated by an ion-exchange membrane was used to segregate an organic catholyte for EC and an aqueous anolyte for OER. Specifically, to study the effect of a membrane type on the outcome of EC reaction, we tested (1) a CEM based on a chemically stabilized perfluorosulfonic acid/ poly(tetrafluoroethylene) copolymer in its protonated form, (2) an AEM with high proton blocking capability based on polyaromatic structure with quaternary ammonium bromide, and (3) a BPM consisting of an anion

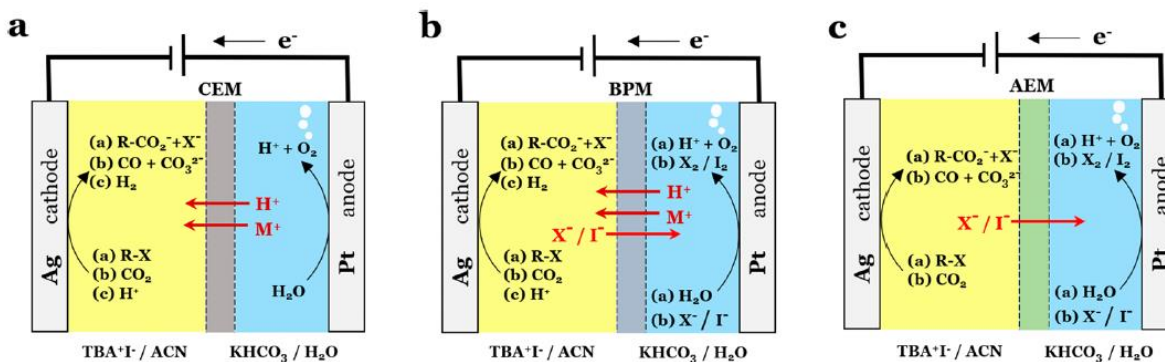


Figure 3. 2: Cell view and ion transport in EC/OER reactions performed in a divided cell with the Ag cathode, R–X/TBAI/ACN catholyte, Pt anode, KHCO₃/H₂O anolyte, and CEM (a), BPM (b), or AEM (c). Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

exchange layer and a cation-exchange layer (Figure 3.2).¹⁷⁸ For all three types of membranes, we performed electrolysis using a CO₂-saturated organic electrolyte (tetrabutylammonium iodide in acetonitrile, TBAI/ACN) containing R–Br (1-bromoethyl)benzene) in the cathodic compartment and aqueous potassium bicarbonate buffer in the anodic compartment. A nanostructured Ag electrode¹⁷⁹ Figure 3.3 prepared by chemical vapor deposition was selected as cathode due to its higher activity in EC of R–Br compared to other metals,¹⁵⁸ and a Pt mesh was used as a standard OER anode. The distributions of reaction products and current stability (Figure 3.4) were assessed at various fixed potentials.

First, to select meaningful potentials for the potentiostatic tests, we performed CV of a pure electrolyte (Ar saturated), the electrolyte with R–Br and CO₂, and the electrolyte containing only one of these two components of EC (Figures 3.4d and 3.5). In agreement with previous reports,^{180,181} the onset potential of CO₂ reduction was approximately –1.5 V vs Ag/Ag⁺ quasi-reference electrode (QRE) and the onset potential of R–Br reduction was ~–0.5 V vs Ag/Ag⁺ (the latter corresponds to one electron transfer to R–Br: E° (RBr/R•) = –0.49 V vs SCE in ACN,¹⁸¹ or ~0.34 V vs Ag/Ag⁺; for conversion see Appendix), but when both CO₂ and R–Br were present in the electrolyte, a rapid chemical reaction between CO₂ and electrochemically generated R[–] (E° (R/R[–]•) ≈ –0.97 V vs SCE; ~–0.82 V vs Ag/Ag⁺)¹⁵⁸ was evident from a significantly higher current at potentials below ~–1 V vs Ag/Ag⁺ compared to the CV lines of single components.¹⁸² Two reduction peaks were observed in CV scans of R–Br in the CO₂-saturated electrolyte (RBr

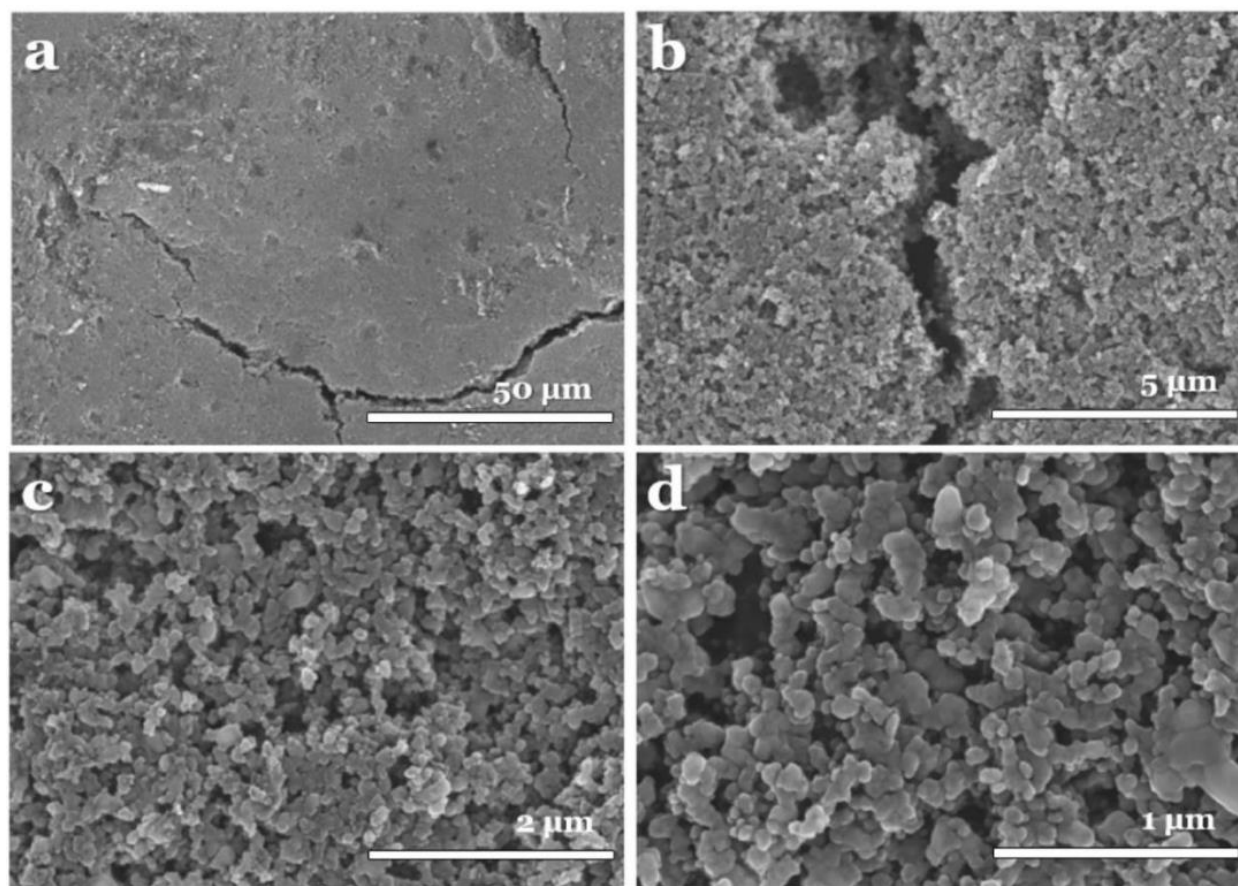


Figure 3. 3: SEM images of the surface of the nanostructured Ag cathode (prepared by chemical vapor deposition) at different magnification. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

$\rightarrow R^\bullet$ at ~ -0.85 V; $R^\bullet \rightarrow R^-$ at ~ -1.2 V), while they overlapped in the Ar-saturated electrolyte. The separation of these peaks in the presence of CO_2 can be explained by faster kinetics of the second reduction step in the presence of CO_2 .¹⁸² Thus, we identified three potential ranges (Figure 3.5): (a) $E_1 > -1.0$ V, where reactions of $R^\bullet$ are dominant; (b) -1.5 V $< E_2 < -1.0$ V, which is promising for chemical fixation of CO_2 by R^- ; and (c) $E_3 < -1.5$ V, where direct CO_2 reduction can occur. Consequently, we selected three potentials from these ranges for testing the membranes performance: -0.8 , -1.4 , and -1.7 V vs Ag/Ag⁺. Figure 3.6 shows the distribution of major electrochemical products in the liquid phase obtained at these three potentials using different membranes and an arbitrary concentration of R-Br (50 mM). The reactions occurred in the diffusion-controlled regime at this R-Br concentration as confirmed by a linear relationship between the current and square root of scan rate (Figure 3.7).¹⁸³ The product distribution was

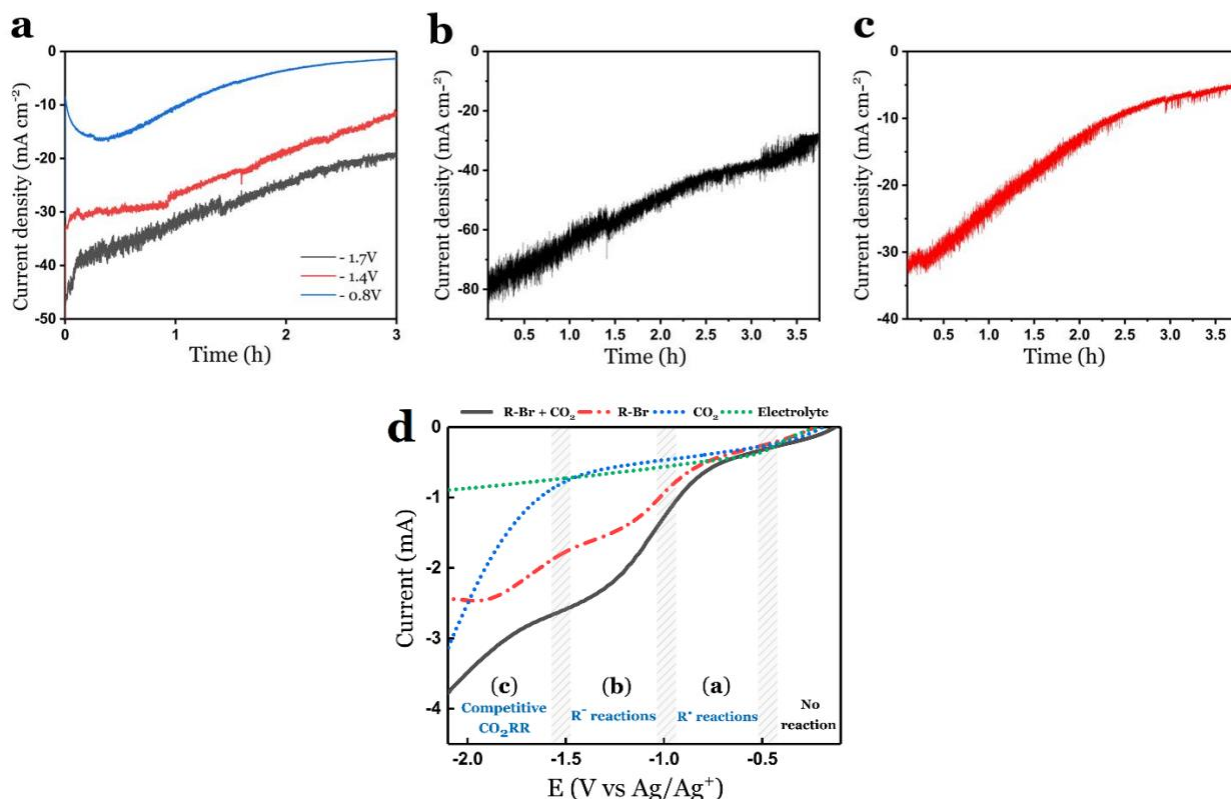


Figure 3. 4: (a) Chronoamperometry (CA) plots for the electrolysis of 50 mM R-Br in 0.1 M TBAI/ACN saturated with CO₂ at different potentials. Examples of full CA plot for the electrolyses of 50 mM R-Br in 0.1 M TBAI/ACN saturated with CO₂ at -1.7 V (b) and -1.4 V (c). (d) Determination of potential ranges: cathodic sweeps of CV recorded at 200 mV sec⁻¹ scan rate at Ag in (a) Ar-saturated ACN + 0.1 M TBAI; (b) CO₂-saturated ACN + 0.1 M TBAI; (c) Ar-saturated ACN + 0.1 M TBAI + 25 mM (1-bromoethyl)benzene; (d) CO₂- saturated ACN + 0.1 M TBAI + 25 mM (1-bromoethyl)benzene. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

determined by ¹H NMR analysis of reaction mixtures using an internal standard (Table 3.1 and Figure 3.8). As a result of EC, carboxylate RCO₂⁻ or its ester RCO₂R [via S_N2 reaction of RCO₂⁻ with R-Br] was formed. Combined yields and FEs of RCO₂⁻ and RCO₂R (EC products) represent the EC selectivity in the electrolysis. Other organic products of electrochemical nature^{144-149,184} included dimer R-R, alcohol R-OH, ether R-O-R, and alkylarene R-H. Other side products, such as alkenes and their oligomers,^{176,177,185} can be formed as a result of nonelectrochemical transformations of reactive intermediates produced during electrolysis and are not included in Figure 3.6. At -0.8 V vs Ag/Ag⁺ with AEM, the only electrochemical product was R-R (86%

yield). At a less negative potential (-0.6 V), R–R was obtained in 95% yield and with 96% FE (Table 3.2) due to the suppression of undesirable side processes, such as elimination reactions catalyzed by Br^- generated during the electrolysis.^{176,177} Thus, we demonstrated that the selective

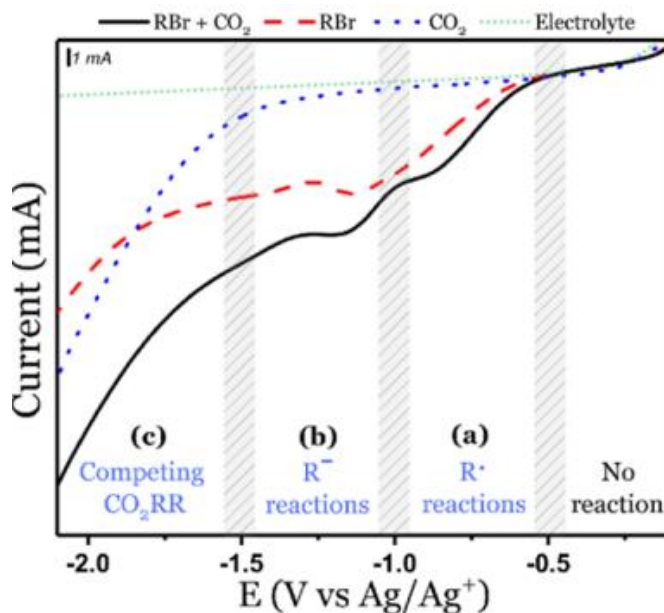


Figure 3. 5: Determination of potential ranges: cathodic sweeps of CV recorded at 50 mV s^{-1} scan rate at Ag in Ar-saturated ACN + 0.25 M tetrabutylammonium bromide (TBABr); CO_2 -saturated ACN + 0.25 M TBABr; Ar-saturated ACN + 0.25 M TBABr + 25 mM (1-bromoethyl)benzene; CO_2 -saturated ACN + 0.25 M TBABr + 25 mM (1-bromoethyl)benzene. (a) $E_1 > -1.0$ V: reactions of $\text{R}^\bullet$; (b) $-1.5 \text{ V} < E_2 < -1.0$ V: reactions of R^- ; and (c) $E_3 < -1.5$ V: direct CO_2 reduction. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

C–C coupling of organic halides can be performed at low potentials in divided cells with AEM. In contrast, at -0.8 V vs Ag/Ag^+ with BPM and CEM, besides R–R, ester R–OR and ethylbenzene R–H were formed, with $[\text{R–R}]/[\text{R–OR}]/[\text{R–H}]$ ratios observed with all three membranes. However, AEM showed the best selectivity with [EC of 8:1:2 (CEM) and 7:1:2 (BPM)]. At -1.4 V vs Ag/Ag^+ , the formation of EC products was observed with all three membranes. However, AEM showed the best selectivity with [EC products]/[R–R]/[R–OH] ratio of 1.6:1:0.2. In the case of CEM and BPM, [EC products]/[R–R] ratio dropped to 0.7:1 and 0.3:1, respectively, in addition to the formation of R–OH, R–H, and R–OR. At -1.7 V vs Ag/Ag^+ , EC selectivity improved with all membranes and [EC products]/[R–R] ratio increased to 2.8:1, 2.8:1, and 2:1 for AEM, CEM,

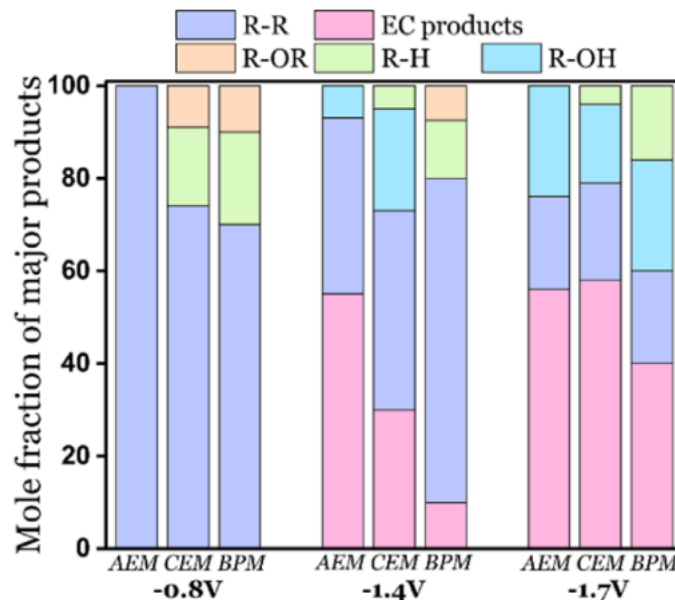


Figure 3. 6: Initial assessment of the membranes at an arbitrary (50 mM) precursor concentration. Bar graph shows the distribution of major liquid products in the electrolysis of 50 mM R-Br in CO₂-saturated ACN + 0.1 M TBAI in a divided cell with AEM, CEM, or BPM at -0.8, -1.4, and -1.7 V. The product distribution is shown as a molar fraction of their sum, i.e., [EC products] + [R-R] + [R-OR] + [R-H] + [R-OH]. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

and BPM, respectively. The formation of R-H was observed only with CEM and BPM membranes, due to proton transfer from the anodic compartment, which was absent in the case of

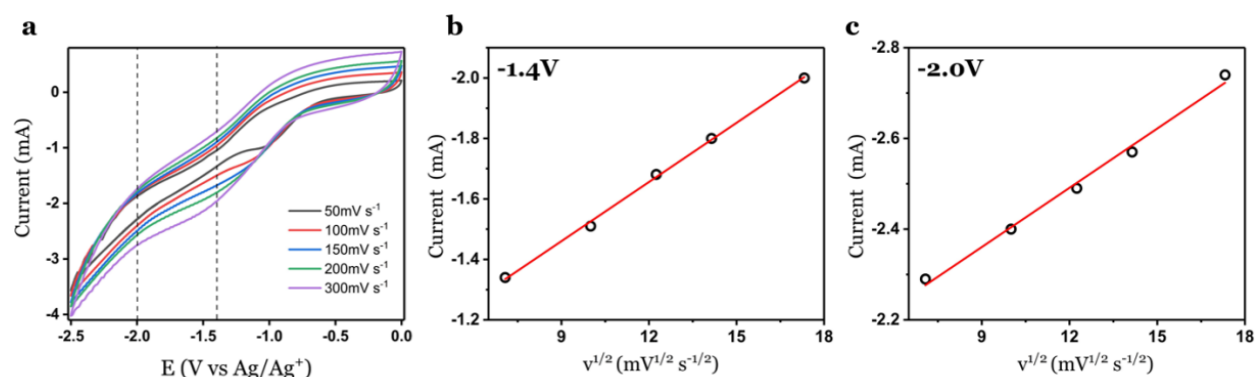


Figure 3. 7: (a) CV plots recorded at different scan rates ($v = 50, 100, 150, 200$ and 300 mV s^{-1}) at Ag electrode in 50 mM R-Br in 0.1 M TBAI/ACN saturated with CO₂. (b,c) Linear correlation of current and square root of scan rate for -1.4 V (b) and -2.0 V (c). Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

Table 3. 1: Product identification based on the peak values for EC of R-Br compared to the peak values for known compounds. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

Electrochemical reduction products			Assignment		Known Standards		
Chemical shift	¹ H Splitting	J coupling	Probed Nucleus	Product type	Chemical shift	¹ H Splitting	J coupling
<i>After work-up procedure (without electrolyte)</i>							
5.90	qd	6.6, 3.8 Hz	Ph(Me) CH -O ₂ CR	RCO₂R [1]	5.85	q	6.6 Hz
3.79	q	7.2 Hz	RO ₂ C- CH (Me)Ph		3.73	q	7.2 Hz
1.54	d	7.2 Hz	Ph(Me)CH-O ₂ CH(Me)Ph		1.47	d	7.2 Hz
1.46	d	6.6 Hz			1.40	d	6.6 Hz
3.78	q	7.2 Hz	Ph(Me) CH CO ₂ H	RCO₂H [3]	3.72	q	7.2 Hz
1.55	d	7.1 Hz	Ph(Me)CHCO ₂ H		1.49	d	7.2 Hz
2.98	m	-	Ph(Me) CH-CH (Me)Ph	R-R [4]	2.95	m	-
2.84	m	-			2.80	m	-
1.32	dd	5.0, 1.8 Hz	Ph(Me)CH-CH(Me)Ph		1.28	dd	4.9, 1.9 Hz
1.07	dd	4.5, 2.0 Hz			1.02	dd	4.5, 2.0 Hz
4.95	q	6.4 Hz	Ph(Me) CH -OH	R-OH [7]	4.77	q	6.5 Hz
4.27	m	-	Ph(Me) CHOCH (Me)Ph	R-OR [6]	4.24	q	6.7 Hz
4.45	m	-			4.52	q	6.5 Hz
2.61	q	7.5 Hz	Ph CH₂ CH ₃	R-H [5]	2.63	q	7.6 Hz
<i>Before work-up procedure (analysis of crude reaction mixture with electrolyte)</i>							
5.83	m	-	Ph(Me) CH -O ₂ CR	RCO₂R	5.85	q	6.6 Hz
3.73	m	-	RO ₂ C- CH (Me)Ph		3.73	q	7.2 Hz
3.57	m	-	Ph(Me) CH CO ₂ TBA	RCO₂TBA [2]	3.60	m	-
2.93	m	-	Ph(Me) CH-CH (Me)Ph	R-R	2.95	m	-
2.79	m	-			2.80	m	-
4.89	m	-	Ph(Me) CH -OH	R-OH	4.77	q	6.5 Hz
4.08	q	7.2 Hz	Ph(Me) CHOCH (Me)Ph	R-OR	4.24	q	6.7 Hz
4.37	q	7.2 Hz			4.52	q	6.5 Hz
2.56	q	7.6 Hz	Ph CH₂ CH ₃	R-H	2.63	q	7.6 Hz
7.55	s	-	1,2,4,5-tetrachlorobenzene	standard	7.55	s	-

*Reaction mixtures were analyzed directly after the electrolysis and the solvent removal (before the workup procedure). To prove the composition of reaction mixtures, they were also hydrolyzed with concentrated HCl, and analyzed again by NMR (after work-up procedure; without electrolyte), see the section above for details.

AEM.

While full conversion of R-Br was achieved with AEM at -1.7 V vs Ag/Ag⁺, the use of CEM or BPM led to R-Br conversions below 100%. The visual examination of the cathodes after

Table 3. 2: Potentiostatic electrochemical reduction of (1-bromoethyl)benzene in the presence of CO₂. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

Entry	E, V vs Ag/Ag ⁺	C _{R-Br} , mM	Membrane	Anolyte	Product yields, %							% of liquid products*
					R-CO ₂ Y ^a	R-CO ₂ R	R-R	R-OH	R-H	R-OR	Total	
1	-0.6	100	AEM	0.5M KHCO ₃	-	-	95	-	-	-	95	100
2	-0.8	50	AEM	- " -	-	-	86	-	-	-	86	98
3	-0.8	- " -	CEM	- " -	-	-	51	-	6	6	63	80
4	-0.8	- " -	BPM	- " -	-	-	43	-	6	6	55	70
5	-0.8	100	CEM	0.1M H ₂ SO ₄	-	-	52	-	7	7	66	83
6	-1.4	50	AEM	0.5M KHCO ₃	9	11	20	2	-	-	42	97
7	-1.4	- " -	CEM	- " -	7	-	20	5	1	-	33	69
8	-1.4	- " -	BPM	- " -	4	-	28	-	5	3	40	59
9	-1.7	- " -	AEM	- " -	5	22	12	7	-	-	46	100
10	-1.7	- " -	CEM	- " -	11	6	10	4	1	-	32	72
11	-1.7	- " -	BPM	- " -	4	2	5	3	2	-	16	59
12	-1.7	- " -	CEM	0.1M H ₂ SO ₄	4	-	28	-	5	3	40	85
13	-1.7	- " -	BPM	0.1M H ₂ SO ₄	2	-	31	-	5	5	43	70
14	-1.7	100	BPM	1M NaCl	2	-	25	-	4	4	35	59

* Percentage of all organic products in liquid phase was calculated by integrating the aromatic region in ¹H NMR. ^aY=H for CEM and BPM; Y = TBA for AEM.

CEM and BPM electrolysis at -1.7 V vs Ag/Ag⁺ (Figure 3.9d,e) revealed the formation of solid products on their surface (primarily KBr and traces of K₂CO₃), that resulted in significant passivation of the cathodes and a subsequent decay of the reaction rate. In contrast, electrolysis with AEM led to no (at -1.4 V vs Ag/Ag⁺) or minor (at -1.7 V vs Ag/Ag⁺) electrode passivation (Figure 3.9b,c): due to the absence of K⁺ ions in the cathodic compartment (see Figure 3.1), possible insoluble by-products were limited to TBA₂CO₃, but only at potentials above the onset for CO₂ reduction leading to the formation of CO and CO₃²⁻. We note that attempts to minimize the passivation when using CEM or BPM by using 0.1 M sulfuric acid as anolyte led to the decrease in EC selectivity and FE due to competing HER at the cathode (Table 3.2).

Trends in the reaction performance with different membranes can be illustrated by the dependence of passed charge as a function of time, Q(t) (Figure 3.10). We note that the electrochemical performance of the nanoporous Ag electrodes in EC was the same after at least 10 sequential 5 h reactions; therefore, we ascribe observed changes in current to the reaction kinetics or electrode passivation with insoluble salts (Figure 3.9). At -1.7 V vs Ag/Ag⁺ in the case of AEM, the Q(t) plot was close to the ideal scenario of 2e⁻ reduction of R-Br, considering the depletion

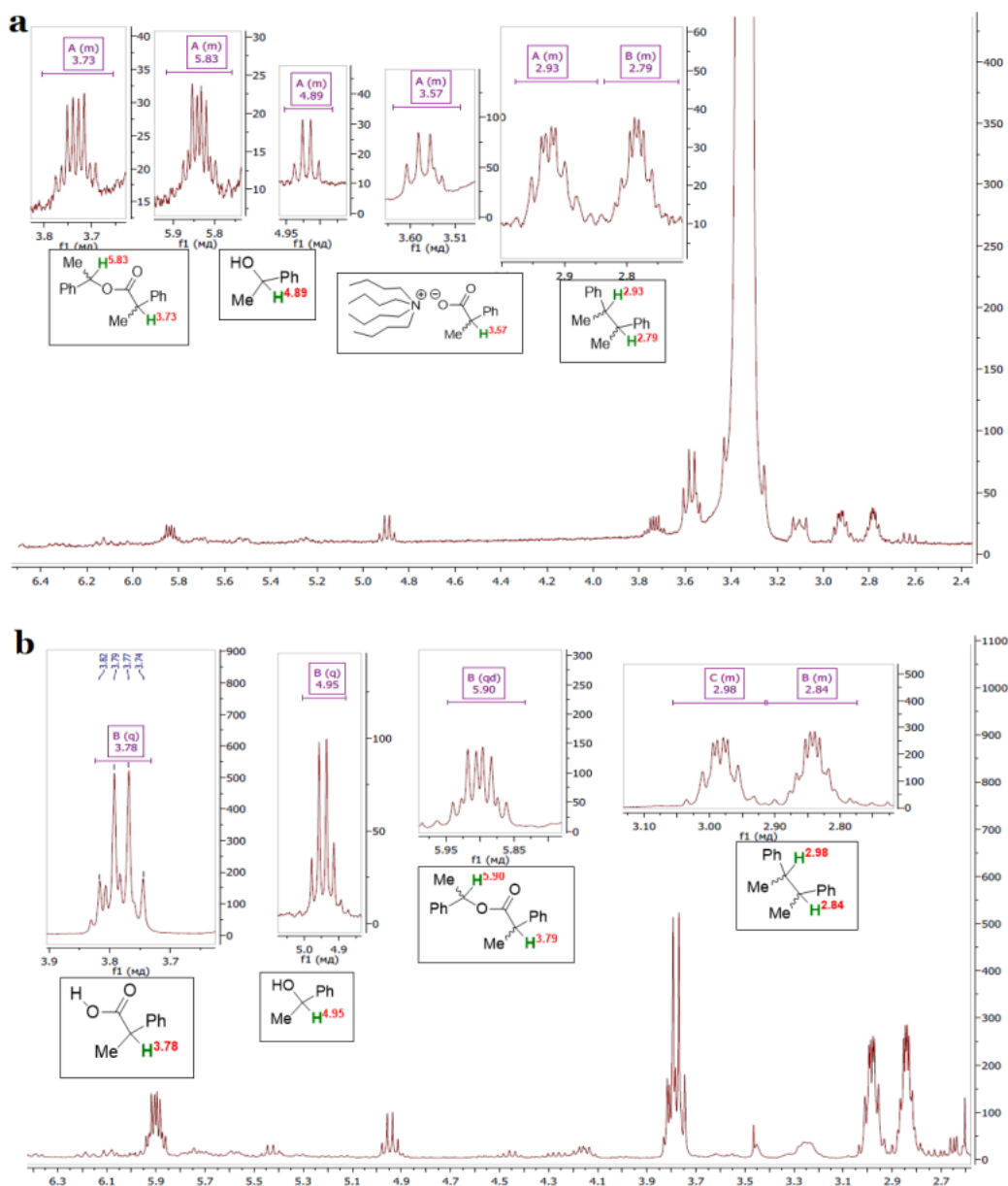


Figure 3. 8: Examples of NMR spectra: (a) crude reaction mixture after the electrolysis of R-Br; (b) reaction mixture after the hydrolysis. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

of R-Br in the course of reaction. When electrode passivation is negligible, the deviation from the calculated trend at later stages of the electrolysis can also indicate a faster than calculated depletion of R-Br, suggesting its participation in nonelectrochemical transformations (e.g., S_N2 reaction with RCO_2^-). In CEM and BPM experiments at -1.7 V (Figure 3.10a), $Q(t)$ curves significantly deviated from the calculated trend, in agreement with the observed cathode passivation. As a result

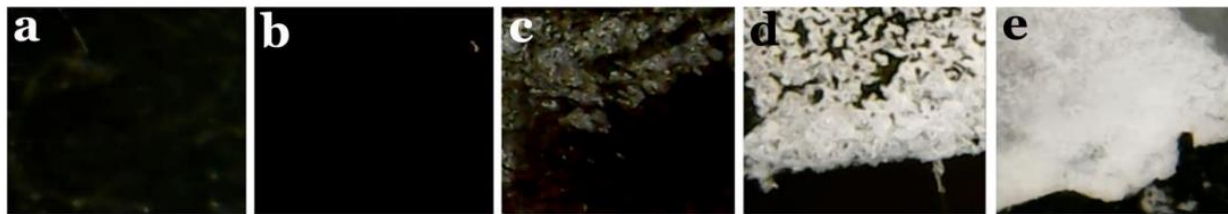


Figure 3. 9: Magnified photographs (image width 0.25 cm) of the electrode surface before (a) and after 5 hours of electrolysis at -1.4 V using AEM membrane (b) showing no change, and at -1.7 V using AEM (c), BPM (d) and CEM (e) showing the cathode surface passivation with solid products. Photographs were taken under similar lighting conditions. Minor formation of TBA_2CO_3 crystals (confirmed by NMR) on the surface of the cathode was observed in the case of AEM (c). Formation of significant amounts of KBr with traces K_2CO_3 passivating the cathodes was observed for BPM and CEM (c, d).

of this drastic decrease in current before the completion of the reaction, only 60–80% conversion of R–Br was achieved with CEM and BPM. At less negative potentials (-1.4 and -0.8 V vs Ag/Ag^+), cathode passivation with BPM was noticeably lower and full conversion of R–Br could be achieved. Poor performance of CEM with respect to R–Br conversion was observed at all tested potentials (Figure 3.11). Importantly, electrolysis with AEM at less negative potentials closely followed the calculated trends of 2e^- and 1e^- reduction of R–Br at -1.4 and -0.8 V vs Ag/Ag^+ , respectively (Figure 3.10b). This information is important for further elucidation of the reaction mechanisms in different potential ranges.

Another noteworthy difference in the performance of the membranes is related to the oxidation process at the anode. Since TBAI was used in the cathodic compartment, OER observed at the anode in the beginning of electrolysis was ultimately replaced by iodine formation when AEM and BPM were used. The ion transport and corresponding side reactions responsible for the observed product distribution variation with different membranes are summarized in Figure 3.2. In the beginning of electrolysis, only two processes are possible at the cathode with all three membranes: R–X reduction and CO_2 reduction, which generate anions RCO_2^- , R^- , X^- , and CO_3^{2-} . Stabilization of these anions in the case of CEM is performed by H^+/K^+ transferred from the anodic side (Figure 3.2a). Carboxylate anions RCO_2^- combine with protons producing the target acid, while the inorganic anions form insoluble potassium salts KX ($\text{X} = \text{Br}, \text{I}$) and K_2CO_3 , which passivate the cathode. In the case of AEM (Figure 3.2c), stabilization of anions can only be

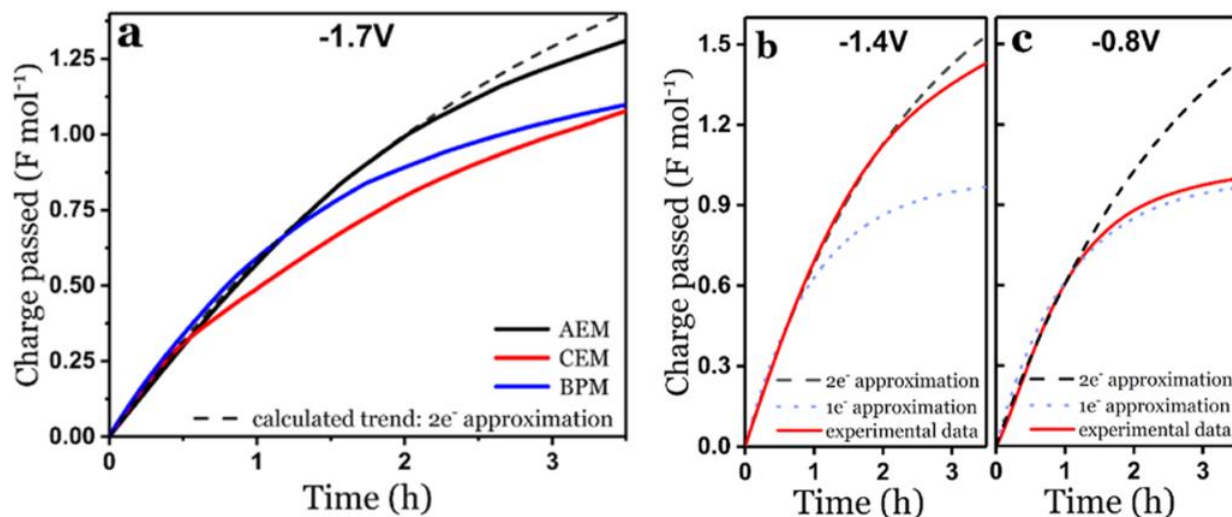


Figure 3. 10: Assessment of electrolysis stability and kinetics. (a) Performance of different membranes at -1.7 V: calculated and measured reaction rate decays during the electrolysis of 50 mM R-Br in ACN + 0.1 M TBAI in a divided cell at -1.7 V with AEM, CEM, and BPM. Experimentally observed trends (solid lines) at -1.4 V (b) and -0.8 V (c) during electrolysis of 50 mM R-Br in ACN + 0.1 M TBAI with AEM, and calculated rate decays considering $1e^-$ (dotted lines) and $2e^-$ (dashed lines) reduction of R-Br. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

performed with TBA⁺ cations, while I⁻ from the electrolyte along with Br⁻ from the starting organic bromide passes through the membrane to the anodic compartment. The initially negligible concentration of these anions in the anolyte gradually increases in the course of electrolysis. With enough I⁻ in the anolyte, iodine formation dominates over OER due to a lower oxidation potential of iodide anions compared to that of water (0.54 and 1.23 V vs SHE, respectively).¹⁸⁶ To maintain OER at the anode, electrolytes with less reactive anions such as Br⁻ or ClO₄⁻ can be used. In the case of BPM (Figure 3.2b), all of the processes described above take place. Despite BPM combining the properties of both CEM and AEM, its efficiency and selectivity were the lowest (Figure 3.6). High yields of protonation product R-H were detected at all potentials, along with low yields of EC products and low R-Br conversion (Table 3.2). This low performance of BPM could be associated with enhanced water dissociation in the membrane layers¹⁸⁷ and membrane degradation due to the delamination of the layers in the organic-aqueous system.¹⁸⁸ Since AEM showed the best overall performance, further investigation of the effect of reaction parameters on

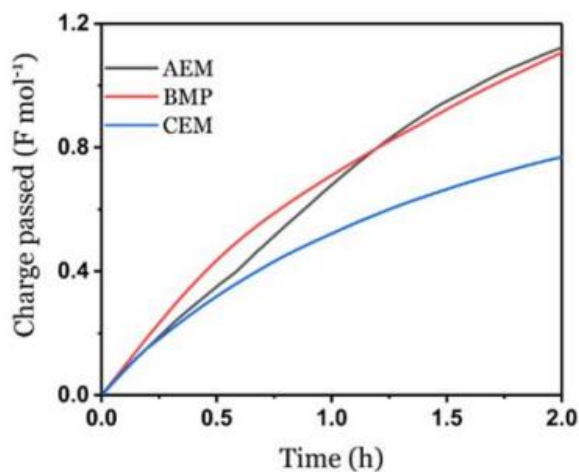


Figure 3. 11: Deterioration of the reaction rate due to the passivation of the cathode surface during the electrolysis of 50 mM R-Br in the 0.1 M TBAI saturated with CO₂ in a divided cell with AEM, CEM and BPM at -1.4 V. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

the course of electrolysis was performed using this membrane. We note that AEM also showed good stability for at least 50 h of continuous or sequential electrolysis without any significant visual changes or decrease in reaction selectivity.

3.3 Effect of reaction parameters on the EC outcome

3.3.1 Effect of the applied potential

The series of electrolyses of R–Br at different cathode potentials were performed to assess the potential influence on the product distribution in more detail (Figure 3.12a). The dimer R–R was the major product (yields up to 86%) at $E > -1.4$ V vs Ag/Ag⁺. The yield of R–R significantly decreased at more negative potentials approaching 0 at -2 V vs Ag/Ag⁺ (only trace amounts were detected by NMR). EC products dominated at -1.8 V vs Ag/Ag⁺ (35%) and -1.6 V vs Ag/Ag⁺ (45%) at 50 and 25 mM concentrations of R–Br, respectively. The higher yield of EC products along with the lower yield of R–R at a lower starting R–Br concentration (while CO₂ concentration remained constant) at almost all potentials points at the importance of optimizing the [R–Br]/[CO₂]

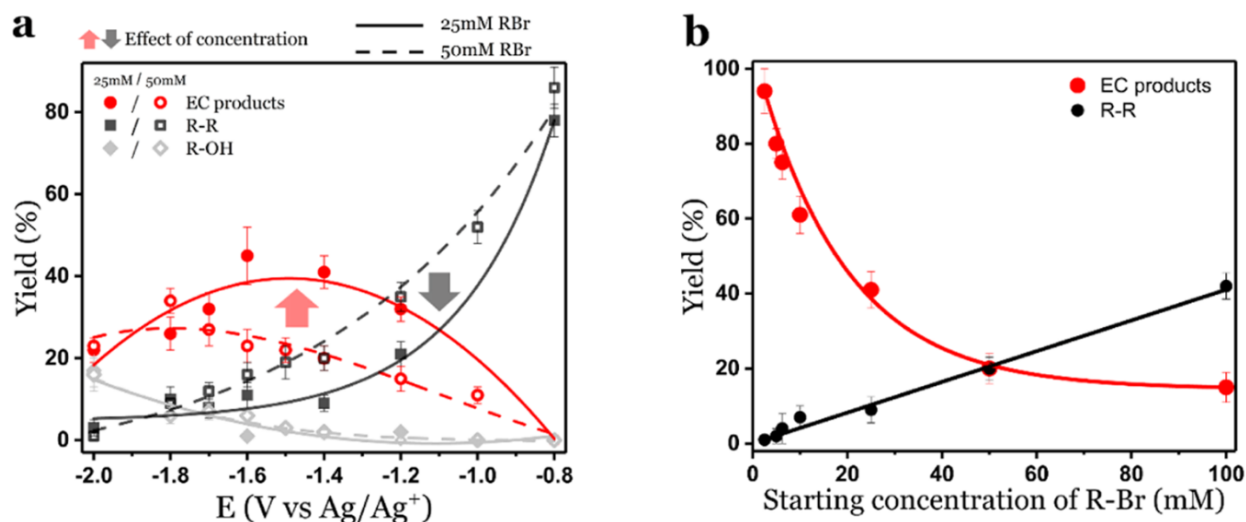


Figure 3. 12: Trends in the major product distribution based on applied potentials and starting R–Br concentrations. (a) Yields of the major products in the electrolysis of 50 mM (empty markers) and 25 mM (solid markers) R–Br (AEM) as a function of applied potential. (b) Yields of the major products at -1.4 V (AEM) as a function of the initial concentration of R–Br. Error bars correspond to standard deviations. The lines are given for eye guidance. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

ratio to maximize the EC yield. Besides R–R and EC products, the formation of R–OH was also observed at potentials more negative than -1.5 V vs Ag/Ag⁺ with maximum yield at -2 V vs Ag/Ag⁺ (16%). The yield of the R–OH was similar at both concentrations. Since R–OH formation

requires the presence of H₂O in the reaction medium,¹⁸⁹ this observation suggests that at potentials below -1.6 V vs Ag/Ag⁺ water starts to pass through AEM; therefore, applicable potentials for EC in ACN/AEM/water system lay above this potential value.

3.3.2 Effect of the starting precursor concentration

To further elucidate the influence of the initial R-Br concentration on the product distribution, a series of electrolyses of R-Br with different initial concentrations (from 2.5 to 100 mM) were performed at -1.4 V. Figure 3.12b shows that the lower the starting concentration of R-Br, the lower the yield of R-R, with an almost linear trend. The formation of side products (appearing as additional signals between 3.5 and 6.5 ppm in the NMR spectra of the reaction mixture; see Figure 3.8) was also noticeably suppressed at lower starting R-Br concentrations. Consequently, the yield of EC products increased nearly exponentially with the decreasing concentration of the precursor. These trends indicated that at low concentrations of the R-Br radical coupling and nonelectrochemical side reactions were suppressed. The nature of the effect is closely related to the ratio between CO₂ and R-Br (or its reduction intermediates) in the reaction mixture: if CO₂ is readily available once R⁻ is formed, the following nucleophilic addition (Ad_N) proceeds selectively with the formation of the corresponding carboxylic anion (RCO₂⁻). In addition, with the decrease in concentration, a maximum yield of EC products was observed at less negative potentials, due to a higher contribution of direct CO₂ reduction to CO (Figure 3.13).^{170,171} Overall, the maximum yields of EC products were achieved with AEM at -1.4 V vs Ag/Ag⁺ in dilute solutions (up to quantitative at 2.5 mM). Although in dilute R-Br solutions R-R formation could be completely suppressed, other side reactions were still observed due to the increased ratio of water traces (from the anolyte) and reactive anion R⁻ generated in EC in the reaction mixture, in addition to a higher contribution of competing CO₂ reduction.

3.3.3 Effect of the charge passed

Considering the effects described above and gradual depletion of the starting material in the course of the reaction, we examined how the reaction selectivity was changing in time with the charge passed. The contribution of direct CO₂ electroreduction to CO and its impact on the selectivity of EC with R-Br depletion were also investigated. We note that only minimal contribution of direct CO₂ reduction is expected at -1.4 V vs Ag/Ag⁺, as it is above the apparent

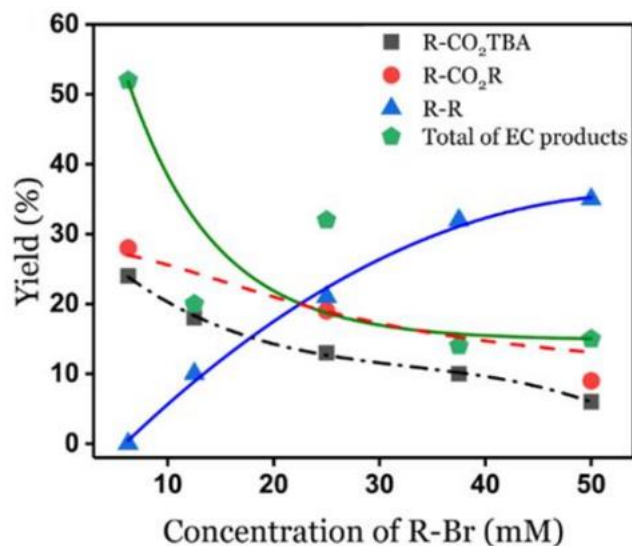


Figure 3. 13: Yields of major products of the electrolysis of 25 mM R-Br in the presence of CO₂ as a function of the applied potential. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

onset potential for CO₂ reduction, according to CV sweeps (Figure 3.5). In addition, the membrane separating aprotic organic and aqueous electrolytes could allow traces of water to cross over, resulting in subsequent HER at the cathode. The distribution of gas products (CO and H₂) as a

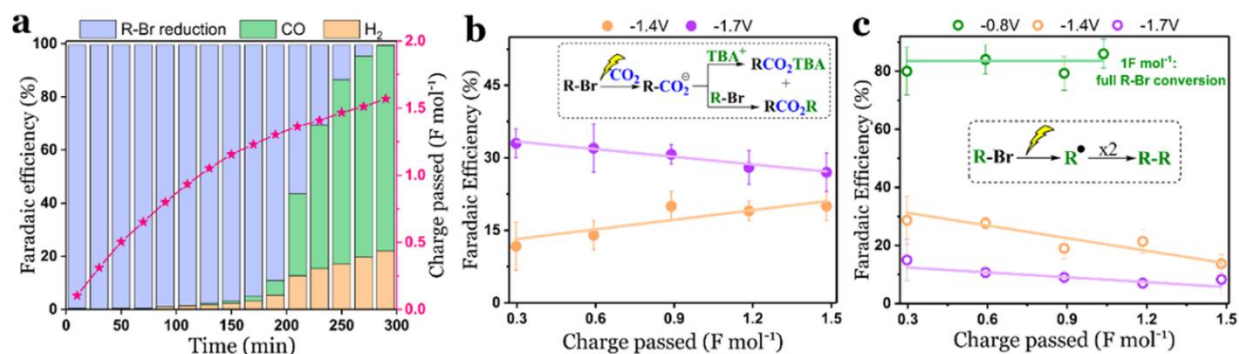


Figure 3. 14: Evaluation of consistency of product distribution in the course of electrolysis. Product distribution during electrolysis of 50 mM R-Br with AEM: (a) FEs of gas and liquid products (GC data) and charge passed in time at -1.4 V showing the effect of R-Br depletion on the process. (b, c) FEs of EC products (b) and R-R (c) as a function of charge passed for electrolysis at different potentials. Error bars correspond to standard deviations. The lines in (b) and (c) are given for eye guidance. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

function of reaction time was evaluated using in-line gas chromatography (GC) analysis (Figure 3.14a) in a series of electrolyses of 50 mM R-Br in the presence of CO₂ at different potentials (−0.8, −1.4, −1.7, −2.2 V vs Ag/Ag⁺; Figure 3.15). With respect to gas products, at −1.4 V vs Ag/Ag⁺, FEs of CO and H₂ were < 1% until the depletion of R-Br, indicating the dominance of the R-Br reduction over the direct CO₂ reduction and HER. With the depletion of R-Br, FEs of gas products started to grow and reached maxima (FE_{CO} = 78% and FE_{H₂} = 22%) after the full consumption of R-Br (note significantly lower currents compared to the average for the EC duration; Figures 3.14 and 3.4b). At a less negative potential (−0.8 V vs Ag/Ag⁺; Figure 3.15a), the formation of gas products was suppressed, and R-Br reduction was the major process. At more negative potentials (−1.7 and −2.2 V vs Ag/Ag⁺; Figure 3.15b,c), R-Br reduction was still the dominant process over CO and H₂ formation initially, although CO formation was observed earlier and at higher partial current density values. To understand the main changes in the distribution of major liquid products in the course of electrolysis, the reaction mixtures were analyzed by ¹H NMR after passing every 0.3 F mol^{−1} until the completion of the reaction (Figures 3.14b,c and 3.16). At −0.8 V vs Ag/Ag⁺, the formation of EC products was not observed, and FE of R-R was constant until complete R-Br consumption after passing 1.0 F mol^{−1}. At more negative potentials (−1.4 and −1.7 V vs Ag/Ag⁺), FEs of R-R were initially lower and gradually dropped with the electrolysis time (Figure 3.14c). This behavior was associated with the decrease in R-Br concentration in the course of electrolysis, in agreement with the suppression of the dimerization reaction observed in dilute R-Br solutions (Figure 3.12b). With respect to EC product distribution in time at more negative potentials, it gradually increased at −1.4 V vs Ag/Ag⁺ (consistent with the decrease in

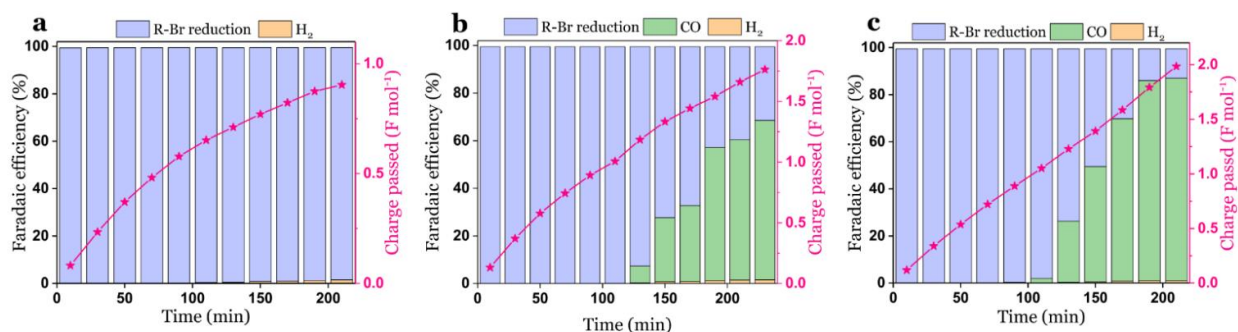


Figure 3. 15: Distribution of FEs of gas and liquid products (derived from GC data) and charge passed in time of electrolysis of 50 mM R-Br at -0.8 V (a), -1.7 V (b) and -2.2 V (c). Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

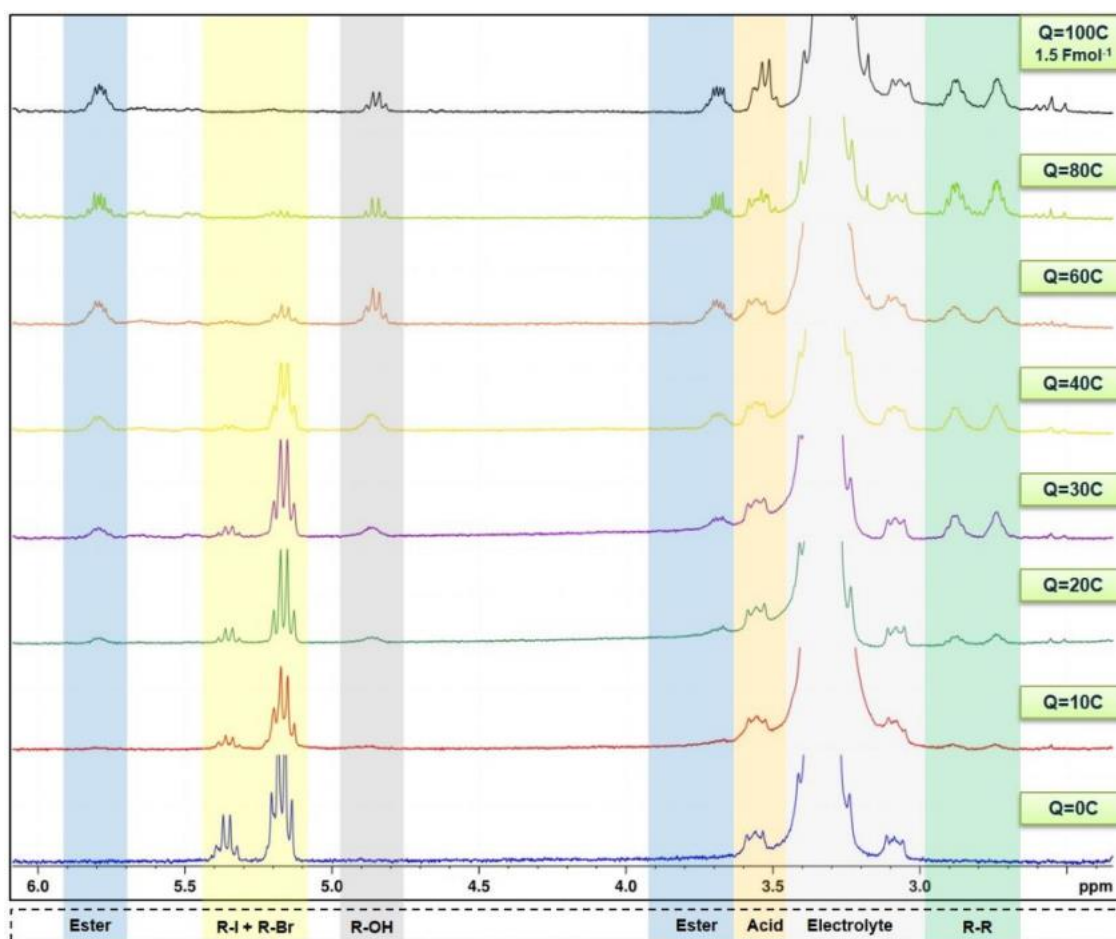


Figure 3. 16: NMR analysis of the reaction mixtures for the electrolysis of 50 mM R-Br at -1.4 V after passing the different amounts of charge compared with the reaction mixture before the electrolysis. Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

FES of R- R), in agreement with the concentration dependence trend, but at -1.7 V vs Ag/Ag^+ , it slightly decreased (Figure 3.14b). This different behavior undefined suggests a variation in the EC reaction mechanism at these two potentials. Indeed, since at -1.7 V vs Ag/Ag^+ CO_2 reduction was more pronounced than at -1.4 V vs Ag/Ag^+ (Figure 3.2), the EC reaction could take place through CO_2 reduction to a radical anion $\text{CO}_2^{\bullet-}$ and its subsequent reaction with R-Br. In this case, a competing process was $\text{CO}_2^{\bullet-}$ disproportionation¹⁹⁰ to CO and CO_3^{2-} which became more prominent with the decreasing R-Br concentration, explaining the reduction in EC product yields with electrolysis progression.

3.3.4 Effect of the temperature

Since the concentration of CO_2 increases with the decreasing temperature, the latter affects the ratio of R-Br (or $\text{R}^\bullet/\text{R}^-$) and CO_2 and consequently the product distribution. Indeed, the electrolysis of 50 mM R-Br at -1.2 V vs Ag/Ag^+ at a reduced temperature favored EC products, with their yields increasing from 15% at room temperature to 30% at $0\text{ }^\circ\text{C}$ (Figure 3.17a), while the yield of R-R dropped from 35 to 27%. At the same time, the combined yield of EC products and R-R was higher at a reduced temperature, indicating that electroorganic side reactions were suppressed (confirmed by NMR). A similar temperature effect was also observed for more negative potentials (Figure 3.17b).

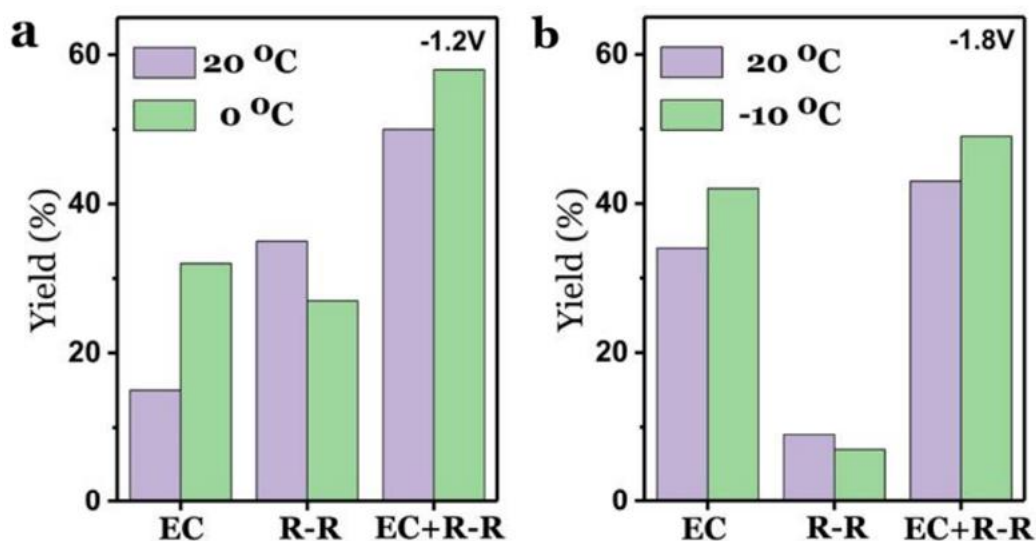


Figure 3. 17: Effect of the temperature on the major product distribution in the electrolysis of 50mM R-Br at -1.2 V (a) and -1.8 V (b). Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society.

3.4 Reaction mechanism in the absence of sacrificial metal anodes

A general mechanism for electroreduction of organic halides and CO₂ in divided cells with nonsacrificial anodes that considers all possible pathways consistent with our experimental data and earlier reports^{140-149,184} is summarized in Figure 3.18. The pathways are separated into blocks according to the following potential ranges: $E_1 > -1.0$ V, corresponding to $R^\bullet$ formation and its subsequent transformations (Figure 3.18a); -1.5 V $< E_2 < -1.0$ V, corresponding to R^- formation and its reactions without competing CO₂ reduction (Figure 3.18b); $E_3 < -1.5$ V, showing the influence of CO₂ reduction on the course of EC of organic halides (Figure 3.18c). The electrochemical R–Br activation starts with the cleavage of the C–Hal bond with the formation of $R^\bullet$, followed by the reduction of the radical to a corresponding carbanion R^- , which then reacts with CO₂.¹⁹¹ The generation of $R^\bullet$ either occurs via the initial formation of radical anion

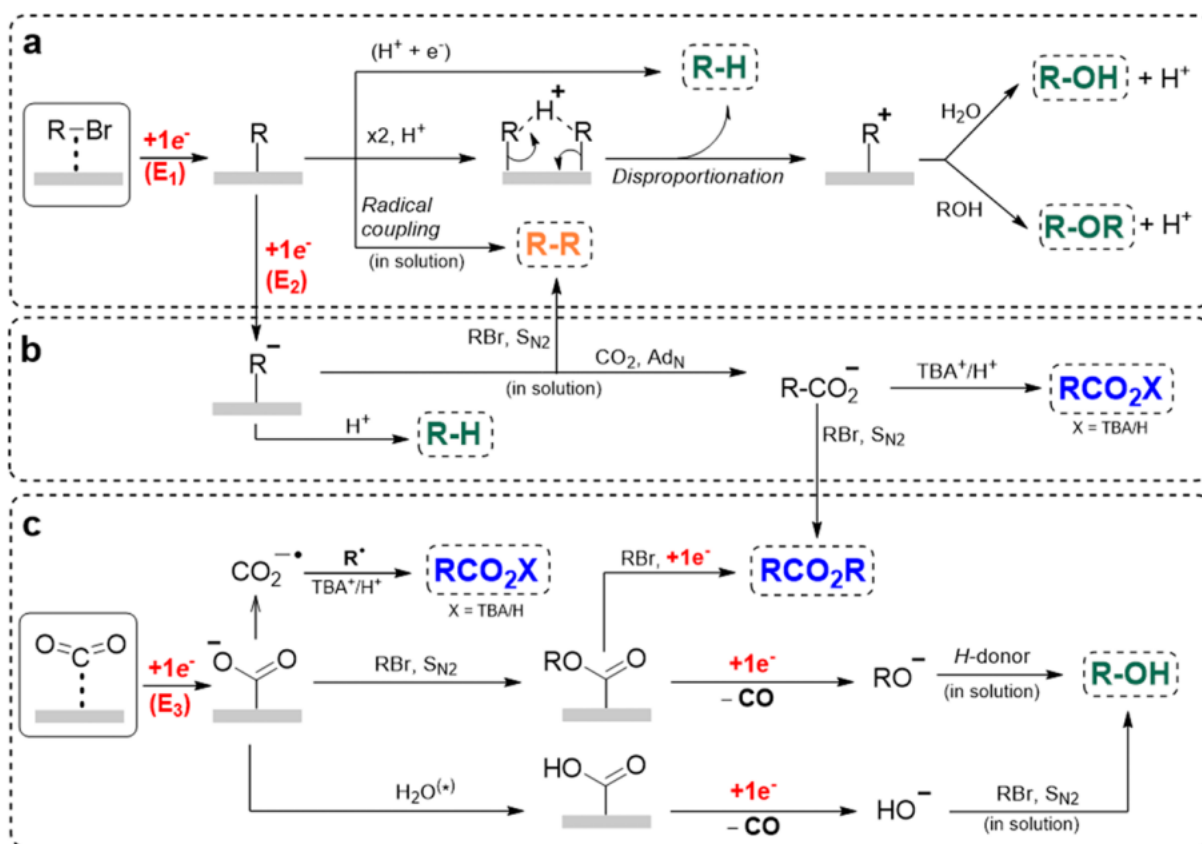


Figure 3. 18: Proposed mechanism and side reactions of electroreduction of organic halides and CO₂ in different potential ranges. (a) $E_1 > -1.0$ V, (b) -1.5 V $< E_2 < -1.0$ V, and (c) $E_3 < -1.5$ V. $CO_2^{\bullet-}$ intermediate can react with CO₂ followed by reductive disproportionation to CO and CO_3^{2-} . Reprinted with permission from ref. [76]. Copyright 2019, American Chemical Society

intermediate $\text{RBr}^{\bullet-}$ followed by the elimination of Br^- ^{158,192} or via a concerted mechanism.¹⁹² Besides the direct electrochemical reduction of the starting bromide, the halogen exchange with electrolyte (TBAI) can also occur.¹⁹³ Indeed, the analysis of the reaction mixture before a full conversion of the starting material (after passing $0.3\text{--}1.2\text{ F mol}^{-1}$) showed the presence of both R-Br and R-I in reaction mixtures (Figure 3.16) with bromide being dominant. Since the standard reduction potential of (1-iodoethyl)benzene is more positive than that for (1-bromoethyl)benzene ($\Delta E \approx 0.15\text{ V}$),¹⁸¹ the presence of I^- in the electrolyte can lower the energy requirement for $\text{R}^\bullet$ generation and thereby decrease the cell potential. At potentials less negative than $E(\text{R}^\bullet/\text{R}^-)$, only radical transformations are possible (E_1 , Figure 3.18a). Indeed, the majority of $\text{R}^\bullet$ underwent the radical coupling reaction, giving the dimer R-R as a main reaction product (up to 95% at -0.6 V vs Ag/Ag^+). Based on DFT calculations, the dimerization likely occurs in solution, as the energy barrier for the radical coupling in solution is lower than on the electrode surface.⁷⁶ Besides dimerization, $\text{R}^\bullet$ can be involved in disproportionation, H-atom abstraction, nucleophilic $\text{S}_{\text{N}}1$ -like reactions, rearrangements, and addition to unsaturated systems (e.g., styrene) originating from the elimination reaction in the starting bromide mediated by different nucleophiles (e.g., Br^-) generated during electrolysis.^{176,177,185,193} The presence of R-H and R-OR in the ratio 2:1 was observed when using BPM and CEM. Typically, the formation of both products is attributed to the R^- transformations in the presence of water or H^+ .¹⁸⁴ Alternatively, the formation of R-H can also be explained by the abstraction of hydrogen atom from the solvent (or any other H donors) by $\text{R}^\bullet$,^{190,194} or via disproportionation.^{194,195} Our experimental results show that the presence of H^+ in the catholyte is critical for the formation of R-H and R-OR , since they were not observed in the AEM experiments at -0.8 V vs Ag/Ag^+ . A constant ratio between these two products indicated that they originated from the initial disproportionation reaction, catalyzed by H^+ (Figure 3.18c). Carbocations R^+ generated during disproportionation react with the traces of water to form R-OH , which subsequently undergoes an alkylation reaction to produce R-OR . At potentials $-1.5\text{ V} < E_2 < -1.0\text{ V}$, the reduction of radicals $\text{R}^\bullet$ to R^- becomes a dominant process (Figure 3.18b), which leads to a dramatic decrease in the R-R yield (Figure 3.12a). The formation of R-R at high negative potentials represents an $\text{S}_{\text{N}}2$ reaction of active anions with the starting R-Br . The $[\text{CO}_2]/[\text{RBr}]$ ratio plays an important role in this process: if the reaction is too fast, the concentration of CO_2 at the cathode surface is not sufficient for it to react with every generated R^- therefore, some of R^- reacts with R-Br or participates in other undesirable side reactions. In dilute R-Br solutions,

CO₂ is present in excess, leading to the suppression of side reactions and a selective formation of the carboxylate anion. The formed RCO₂[−] then reacts with cations, i.e., H⁺ or K⁺ for BPM, CEM, or TBA⁺ for AEM. Since TBA salt is more nucleophilic than the acid, the rate of its S_N2 reaction with R–Br is higher and therefore higher yields of the ester are observed for AEM.^{191,196} At more negative potentials (E₃ < −1.5 V), a significant formation of CO starts only near a full conversion of R–Br. With the increase in [CO₂]/[RBr] ratio associated with the depletion of R–Br, CO₂ reduction to CO occurs through the formation of CO₂^{−•} intermediate.¹⁹⁷ The absence of CO in the beginning of the reaction is likely due to a higher affinity of the Ag cathode to R–Br than CO₂, or due to the reaction of CO₂^{−•} with R–Br (or R•).¹⁹⁵ Specifically, CO₂^{−•} reacting with excess R–Br can form CO₂R• intermediate (similarly to CO₂H• intermediate formation in CO₂ electroreduction in aqueous media).¹⁹⁷ This intermediate can further be reduced with the formation of either CO and ROO[−] anion or CO₂R[−]. The latter is an active carbanion that can react with R–Br to form the ester (Figure 3.18c). DFT calculations of energy barriers for the initial steps of R–Br and CO₂ reduction on the Ag surface show their dependence on the applied potential.⁷⁶ Specifically, at low potentials, the difference is large, with significantly higher barriers for CO₂ reduction, leading to R–Br reduction being the primary departure point for the chemical transformations. At −1.5 V vs SHE (approximately −1.59 V vs Ag/Ag⁺), the trend switches, and at more negative potentials, CO₂ reduction is more favorable than the reduction of R–Br (Figure 3.18).⁷⁶ This result further supports the mechanism differentiation described in Figure 3.18.

3.5 Anodic reaction choice towards lower cell energy

3.5.1 Identification of the anodic reactions of interest

Even though we proved the feasibility of the EC coupling with OER, many challenges remain for our technology to achieve economic viability and penetrate the market.¹⁹⁸ One major hurdle is the high energy requirement to run the electrolyzer.¹⁹⁹ Significant efforts must be dedicated to decreasing the voltage requirement for the cathodic process via electrocatalyst, electrolyte, and cell design.²⁰⁰⁻²⁰³ However, to decrease the overall cell voltage, more efforts need to be focused on the synergetic optimization of both anodic and cathodic processes.

Notably, the OER as the anodic process requires high potentials ($E^0_{\text{OER}} = 1.23 \text{ V vs. RHE}$) and produces low-value O_2 as a product.²⁰⁴⁻²⁰⁶ In order to increase the energy efficiency of the overall cell, cathodic CO_2 electroreduction in aqueous medium has been coupled with several alternative anodic reactions with lower energy requirements²⁰⁶⁻²¹² such as TEMPO-mediated electrooxidation of alcohols,^{208,209} solar-driven oxidative dimerization of 1-phenylethanol,²¹⁰ electrooxidation of NaCl ,²¹¹ dyes,²¹² and glycerol.²⁰⁶

Despite the advantages of all the aforementioned anodic reactions, the electrooxidation of contaminants in wastewater is an underexplored and outstanding candidate for OER replacement. Wastewater is abundant (the global production is $380 \text{ billion m}^3 \text{ year}^{-1}$) and in particular, its major nitrogenous contaminants, urea and ammonia, contain highly energetic chemical bonds.²¹³ Moreover, traditional wastewater treatment techniques are often expensive, energy intensive, and can cause secondary pollution.^{214,215} Hence, coupling anodic wastewater treatment with cathodic CO_2 utilization introduces additional value to the overall process while reducing energetic requirements.²¹²

The composition of wastewater is highly dependent on the source and may include a variety of organic compounds²¹⁶⁻²¹⁹ making its direct electro-oxidation challenging due to the formation of toxic by-products (e.g., ClO_3^- , NO_3^-) and poor performance of the electrodes.^{215,220} However, the oxidation of individual components of wastewater is expected to be more controllable and selective while preventing the formation of toxic by-products. Thus, simpler wastewater mixtures from specific industries may be considered as good candidates for OER replacement.

In particular, wastewater from the massive urea production and dialysis industries are enriched in urea²²¹⁻²²⁴ and ammonia^{225,226} and may be concentrated^{227,228} for subsequent

electrochemical utilization.²²¹⁻²²⁶ Treatment of urea and ammonia-containing effluent is essential to avoid their oxidation to hazardous nitrogen oxides in the atmosphere²²⁹⁻²³¹ and contribution to harmful cyanobacterial blooms²³² which is exacerbated by nitrogenous waste originating from mammalian protein metabolism and agricultural runoff. Moreover, both urea and ammonia are attractive from an energetic standpoint and have shown great potential as a fuel for fuel cells^{224,225} and for electrochemical hydrogen production from water.^{224,226} Thus, there is a strong motivation for the study of electrooxidation of urea and ammonia in combination with electrocatalytic CO₂ utilization.

3.5.2 Thermodynamic requirements for UOR-, AOR-based EC electrolyzers

The efficiency of an electrolyzer for CO₂ utilization *via* EC directly depends on the overall cell potential, which is a sum of the standard cell potential (E_{cell}^0), the kinetic overpotentials of cathodic and anodic half-reactions (η_c and η_a), and the ohmic drop (E_{Ω}) arising from resistance and concentration losses (Figure 3.19a, eqn (1)).²³³ The optimization of each parameter will significantly improve the energy efficiency of the system.²³³ The E_{cell}^0 is the major portion of the overall cell potential that can be calculated from the Gibbs free energy of the overall reaction

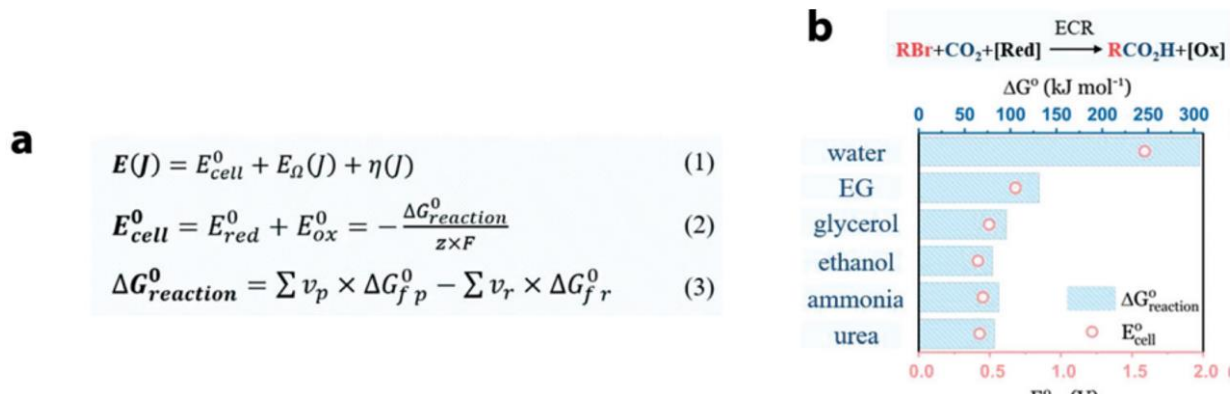


Figure 3. 19: Initial assessment of anodic reaction alternatives to OER. (a) Equations for the reaction energetics calculations, where E_{cell}^0 is the standard cell potential, E_{Ω} is the ohmic drop, η is the sum of cathodic and anodic overpotentials, E_{red}^0 and E_{ox}^0 are the standard potentials for oxidation and reduction processes, v is the stoichiometric coefficient, $\Delta G_{reaction}^0$ is the Gibbs free energy of reaction, and ΔG_f^0 is the Gibbs free energy of formation. (b) Energetics assessment for ECR of RBr coupled to OER, ethanol, ethylene glycol (shown as EG), glycerol, urea, and ammonia electrooxidation. Reprinted with permission from ref. [109]. Copyright 2020, Royal Society of Chemistry.

(Figure 3.19a, eqn (2) and (3)).^{206,234} Specifically, we calculated E_{cell}^0 and ΔG^0 reaction values for AOR and UOR coupled with EC and compared these values with those for several well-known anodic reactions, including OER, ethanol, ethylene glycol, and glycerol oxidation (Figure 3.19b). OER-based electrolyzers showed the highest thermodynamic energy requirements: 306.5 kJ mol⁻¹ and 1.59 V for [EC|OER]. The replacement of OER with alternative anodic reactions decreased the ΔG^0 and E_{cell}^0 by 175–226 kJ mol⁻¹ and 0.9–1.2 V, respectively. The values obtained for UOR and AOR were comparable with that for alcohols, however, the environmental aspect made them more attractive for further investigation. Moreover, except for glycerol, the usage of alcohols for anodic oxidation is counterproductive as they are among the target products of conventional electrochemical CO₂ utilization.^{206,235,236}

The kinetic overpotentials for the half-reactions are the second major factor to be considered. The overpotentials depend on the mechanism of the reaction, the composition and structure of the electrocatalyst, and many other factors.²³⁷ Systematic catalyst design has helped to significantly decrease the overpotentials of cathodic and anodic reactions in the last decade.¹⁰⁹ Specifically, substantial progress has been achieved in OER^{238,239}. For instance, strain stabilized nickel hydroxide nanoribbons decreased η_{OER} to 162 mV.²⁴⁰ In contrast with OER, other anodic reactions have not been as widely investigated and consequently less attention has been devoted to their optimization. The most effective catalysts for AOR and UOR reported to date decreased the corresponding overpotentials only to about 550 mV and 1100 mV, respectively.^{109,218-223}

Based on the analysis of the reported electrocatalysts for AOR and UOR, Pt/Pt-based catalysts and Ni/Ni-based catalysts showed the best performance in AOR and UOR, respectively. Depending on the composition and the structure of the material, the reported anodic potential range was from 0.6 to 0.9 V vs. RHE for AOR (Pt) and from 1.2 to 1.5 V vs. RHE for UOR (Ni). Both ranges were lower than that for OER (from 1.4 to 1.7 V vs. RHE).¹⁰⁹ Considering the use of state-of-the-art catalysts for these anodic reactions, the replacement of OER with UOR or AOR can decrease the cell potential by over 200 mV (Ni) and 800 mV (Pt), respectively.

3.5.3 Experimental evaluation of the EC coupling with UOR and AOR

To assess the feasibility of combining AOR or UOR with EC in aprotic medium, we performed experimental electroanalytical evaluations of their combinations. Coupled electrolysis was performed in a two-compartment H-cell divided by an AEM. The anodic oxidation of ammonia and urea was performed in a 5 M KOH anolyte at commercially available anodes: Ni

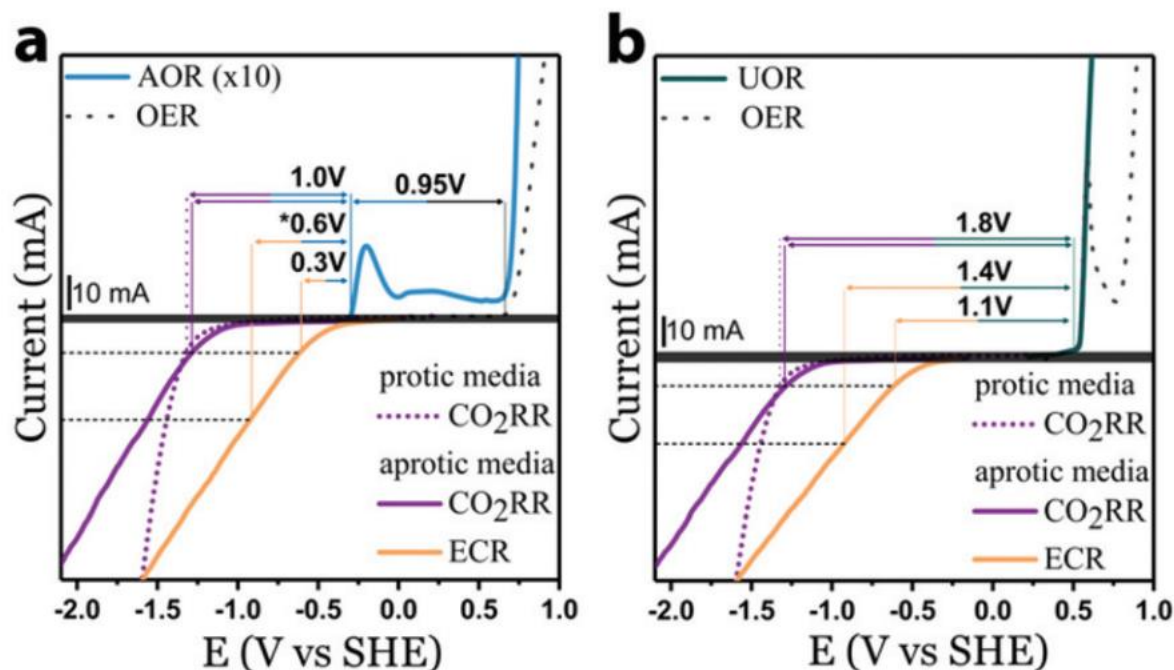


Figure 3. 20: Determination of the minimum required cell potential for ECR and CO₂ electroreduction (cathodic sweeps) coupled with (a) AOR and (b) UOR (anodic sweeps). Cathodic LSV were performed at Ag electrode in: CO₂-saturated 5 M KOH for aqueous CO₂ electroreduction at GDE (dotted purple line); CO₂-saturated ACN + 0.1 M TBABr for aprotic CO₂ electroreduction (solid purple line); CO₂-saturated ACN + 0.1 M TBABr + 25 mM (1-bromoethyl)benzene for ECR (solid orange line). Anodic LSV were performed at (a) Pt and (b) Ni in: 5 M KOH (dotted lines), 5 M KOH + 1 M ammonia (solid line in a), 5 M KOH + 0.33 M urea (solid line in b). All LSVs were acquired at 20 mV s⁻¹ scan rate. CO₂ electroreduction shown as CO₂RR. Reprinted with permission from ref. [109]. Copyright 2020, Royal Society of Chemistry.

foam for urea and Pt mesh or Pt/C for ammonia. The cathodic EC in aprotic media was performed at a carbon-cloth supported Ag nanoparticle cathode with 0.1 M tetrabutylammonium bromide in ACN as catholyte.

First, linear sweep voltammetry (LSV) was performed for the selected cathodic and anodic processes (Figure 3.20). For the EC, the reduction of the (1-bromoethyl)benzene (RBr) occurred at lower potential than that required for direct CO₂ electroreduction. At -0.6 V vs. SHE, RBr undergoes its first electron transfer to produce the corresponding free radical R[•], that is inactive towards CO₂. At -0.9 V vs. SHE R[•] obtains one more electron and nucleophilically attacks CO₂

with the formation of the target carboxylate. Thus, this indirect reduction of CO₂ via EC requires a significantly lower energy input compared to the direct electroreduction of CO₂ in aprotic medium ($\Delta E \approx 400$ mV).

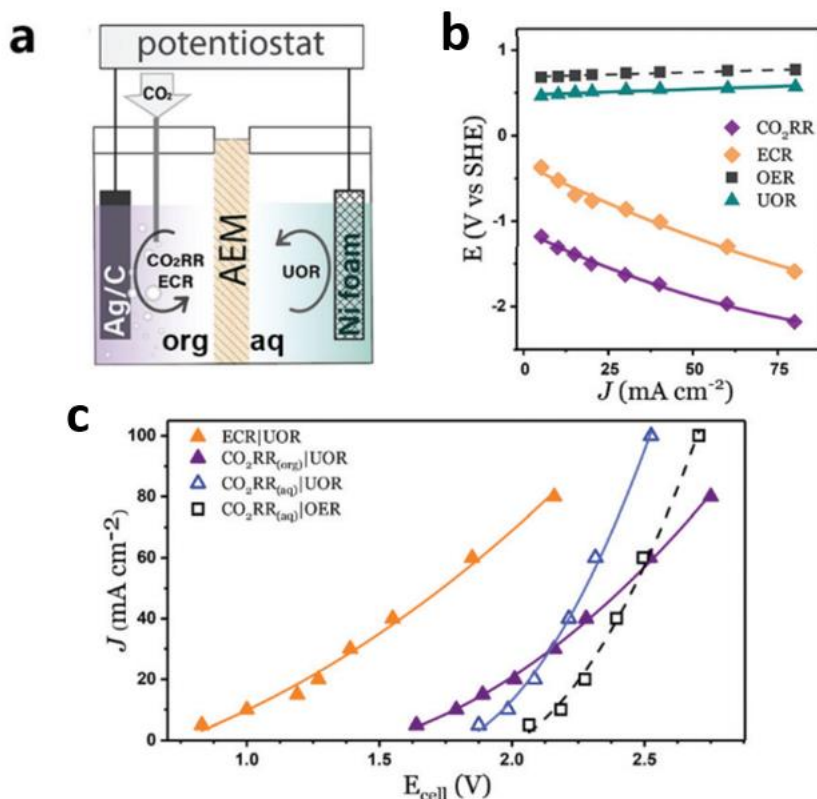


Figure 3. 21: The schematics and performance of [ECR| UOR] and [CO₂ electroreduction|UOR] electrolyzer. (a) An H-cell used for organic [CO₂ electroreduction|UOR] or [ECR| UOR] co-electrolysis. (b) The individual electrode potentials as a function of the total current density. (c) The total current density as a function of the cell potential for the H-cell (CO₂ electroreduction and EC in organic medium as well as and CO₂ electroreduction in aqueous medium in flow electrolyzer). CO₂ electroreduction shown as CO₂RR Reprinted with permission from ref. [109]. Copyright 2020, Royal Society of Chemistry.

The LSV recorded for AOR demonstrated that the oxidation process onset is by 0.95 V lower compared to that of OER under the same reaction conditions. Notably, a durability test showed a significant drop in the activity of the Pt anode towards AOR after each hour of operation due to the poisoning of the surface by N_{ads} intermediates, such as NH_{x,ads} and N_xH_{y,ads}.²⁴¹⁻²⁴⁴ After 4 hours of operation, the Pt catalyst lost activity towards AOR. The fast poisoning of the catalyst

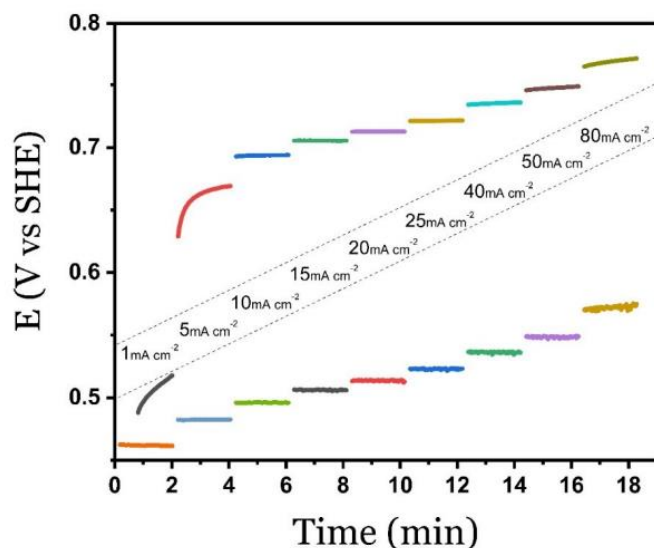


Figure 3. 22: Chronopotentiometry curves for the oxidation of 0.33 M urea and OER at Ni anode in H-cell in 5 M KOH at different current densities (1-80 mA cm^{-2}). Reprinted with permission from ref. [109]. Copyright 2020, Royal Society of Chemistry.

surface (similar to earlier observations in the literature)²⁴⁵⁻²⁵⁰ and small current densities limit the practicality of AOR and indicate the need to develop more durable electrocatalysts with weaker M-N_{ads} bond strength to decrease surface poisoning and facilitate AOR. We have recently

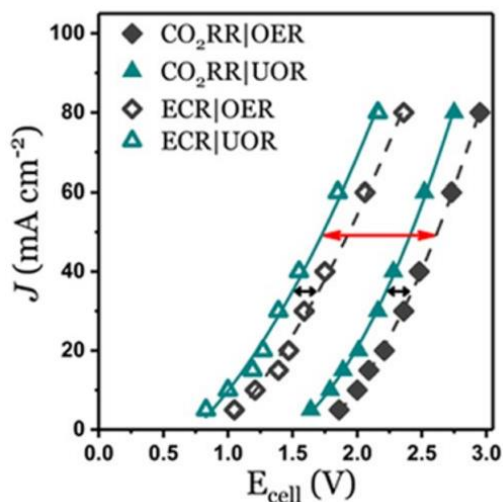


Figure 3. 23: Performance of [CO₂ electroreduction|UOR] and [ECR|UOR] electrolyzers compared with OER-based analogues. Total current density as a function of the cell potential for batch electrolyzer. Reprinted with permission from ref. [109]. CO₂ electroreduction shown as CO₂RR. Copyright 2020, Royal Society of Chemistry.

demonstrated that by sacrificing E_{cell} by about 0.6 V, AOR can be performed on Ni-based electrodes with the impeccable stability of tens of hours of electrolyzer operation.²⁵¹

In contrast to AOR at Pt anode, UOR on Ni electrolysis showed good stability in the anodic performance (no change for over 4 hours). A stable potential was observed at all studied current densities, specifically, 5–80 mA cm⁻² experiments (Figure 3.21 and 3.22). The operating cell potential decreased by 0.2 V in comparison with electrolyzer relying on OER as the anodic reaction (Figure 3.23). Adding the energetical benefits of EC of 0.8 V compared to that of direct CO₂ electroreduction in organic medium, EC coupling with UOR resulted in the total E_{cell} improvement of up to 1 V for a CO₂ utilization strategy in a wide range of applied potentials (Figure 3.23). The potentiostatic cathodic ECR also showed high yields of carboxylation products, i.e., RCO₂H and RCO₂R, of up to 90%, in agreement with the previous report⁷⁶ (86±4% FE and 90% yield of carboxylate for EC).

3.6 Summary

In this chapter, I demonstrated the principal feasibility of performing EC reactions in divided cells with aqueous analytes and nonsacrificial anodes. I laid out the critical role of the membrane separator type and showed that AEM has a superior performance with the highest EC selectivity and the lowest cathode passivation, compared to those of CEM and BPM. This approach opens up the possibility of tuning the overall cell potential by combining electroorganic CO₂ fixation with various anodic reactions and performing the reaction continuously using flow electrolyzers. Importantly, I elucidated the interplay of different reaction pathways in this system and proposed a complete reaction mechanism accounting for all observed products. By optimizing the reaction parameters, I was able to achieve quantitative yields of EC at high [CO₂]/[R-Br] ratios. Moreover, I investigated the minimization of the divided electrolyzer energy requirements by varying anodic reactions. The replacement of standard anodic reaction OER with UOR decreased the overall cell potential by up to 210 mV while increasing the added reaction value. The work included in this chapter paves the way for the design of electrochemical cells for simultaneous C- and N-footprint mitigation by showing the feasibility and benefits of EC-UOR coupled system.

Chapter 4 Catalyst screening for EC in divided systems: bulk materials

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Contribution: Performed conceptualization, investigation, visualization, formal analysis, and assisted with manuscript writing.

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Contribution: Performed material synthesis and characterization.

4.1 Introduction

Historically, EC was widely studied at non-catalytic electrodes, such as glassy carbon.²⁵² In this case, the reduction process can be approximated as an outer-sphere electron transfer yielding in the case of organohalides corresponding radical anions. In contrast, when a metal electrode is used, the reduction usually proceeds through a so called concerted dissociative electron transfer mechanism: R-Hal bond breaking on the metal surface yielding radical R•, while an radical anion is not an intermediate, but rather a transient highly reactive surface-bound specie.²⁵³ Additionally, the strong interaction of R-Hal with an electrocatalyst surface in the transition state significantly lowers the energy requirements for the electron transfer. Consequently, many EC studies were performed with catalytically active metals as cathodes, such as Ag,^{254,257} Cu,²⁵⁵⁻²⁵⁷ Ni²⁵⁵⁻²⁵⁷.

Only a few works attempted to compare the activity of different metal surfaces towards electrochemical reduction of R-Hal.²⁵⁸ In addition, the unavoidable competition of EC with CO₂ electroreduction was poorly studied. Considering the mechanistic differences between conventional and our approaches to EC discussed in Chapter 3, the screening of cathode materials and the assessment of their electrocatalytic activity and selectivity is a crucial next step for the EC optimization in divided electrochemical cells. This chapter aims to summarize electrocatalytic trends for the EC of organohalides and imines on different metal surfaces in sacrificial anode-free systems.

4.2 Electrocarboxylation of benzylic halides

First, we performed cathode screening for a series of benzylic halides. We evaluated performance of 12 bulk metal cathodes and 3 carbon-based materials in EC and CO₂ electroreduction (Figure 4.1a). Moreover, to elucidate the effect of the organic substrate structure on the catalytic activity of these metals, we performed a detailed study of the electrochemical behavior of a series of benzylic halides **1-5** (Figure 4.1b) and CO₂ with each cathode material. This study allowed us to map the potential windows for selective EC on a wide range of cathodic materials.

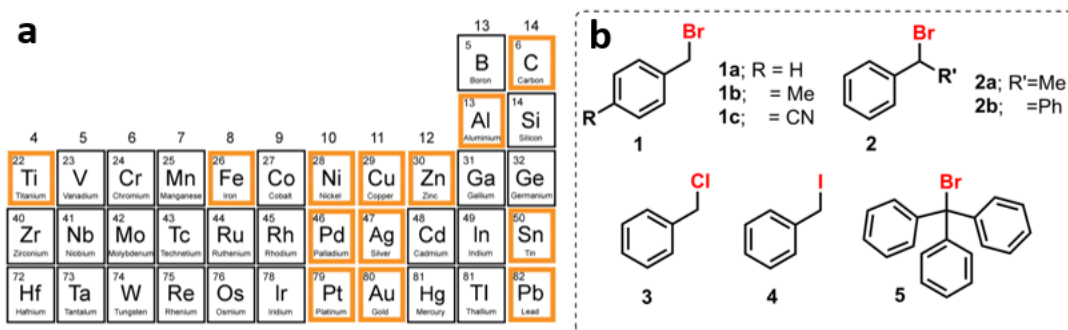


Figure 4. 1: The scope of electrocatalysts screened in the study (a) and molecular structures of the investigated benzylic halides (b). Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

4.2.1 CO₂ electroreduction at different metal cathodes

As generally EC of organohalides *via* the activation of R-Hal requires a lower energy input than EC *via* CO₂ activation, we first set to determine the potential window where the CO₂ activation does not occur. To this end, we investigated the electrochemical behavior of CO₂ at different bulk metal cathodes by performing cyclic voltammetry in a CO₂-saturated CH₃CN containing 0.1 M TEABF₄ (Figure 4.2a,b). The onset potentials for CO₂ ranged from -1.4 V to -1.9 V and no peaks were observed for all metals. Ag, Au, and Pt showed the least negative onset potentials (-1.4 to -1.5 V), followed by Cu, Sn, Zn, and Pd (-1.5 to -1.7 V). Ni, Pb, Fe, Ti, and Al showed the highest energy requirements for direct CO₂ electroreduction ($E_{\text{ons}} < -1.7$ V). A significant difference in CO₂ electroreduction current density values was observed for all metals following the same trend (Figure 4.2c). The highest rates of CO₂ electroreduction were observed for Ag, Au, Pt, Pd and Cu (>18 mA cm⁻² at -2 V), while Zn, Sn, Pb and Fe showed moderate to poor CO₂ electroreduction activity (7-12 mA cm⁻² at -2 V). Al and Ti electrodes did not show any

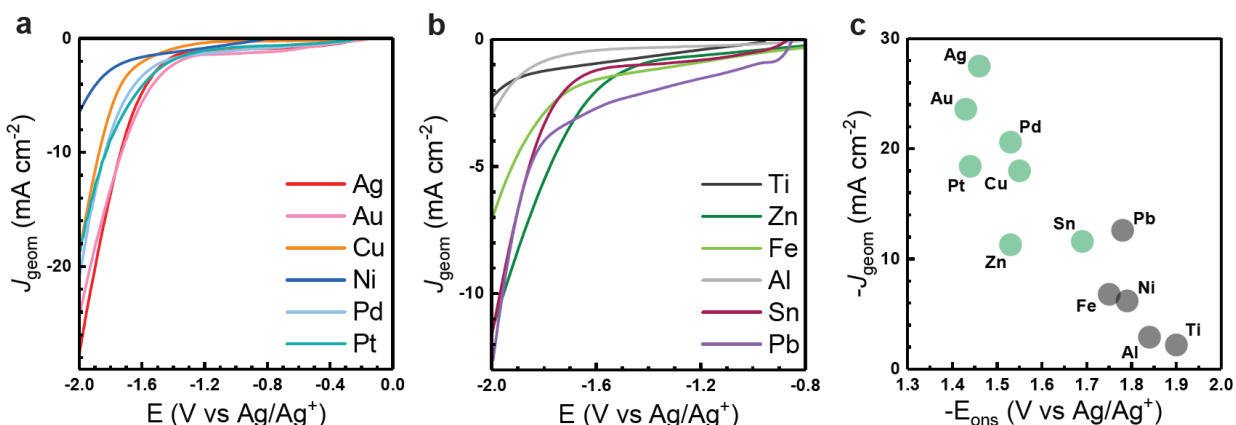


Figure 4. 2: (a,b) Cathodic sweeps of cyclic voltammograms recorded for the reduction of CO₂ in aprotic media. All voltammograms were recorded at 50 mV s⁻¹ scan rate at different bulk metal cathodes (working area ~ 0.2 cm²) in CO₂-saturated CH₃CN–0.1 M TEABF₄. (c) The activity of different metal cathodes towards CO₂ electroreduction (y-axis shows the current density of CO₂ electroreduction at -2 V vs Ag/Ag⁺; x-axis shows the onset potential for direct CO₂ electroreduction); green circles correspond to the electrodes with $E_{\text{ons}}(\text{CO}_2 \text{ electroreduction}) > -1.7$ V, while grey circles correspond to the electrodes with more negative onset potentials for CO₂ electroreduction. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

noticeable CO₂ electroreduction activity in the studied potential range. It is worth noting that Ag, which is a typical catalyst of choice for EC, had the highest activity towards CO₂ electroreduction among the studied metals, meaning that a noticeable contribution of competing CO₂ electroreduction can be expected in EC at this cathode. On the other hand, all screened metals showed a very low to no CO₂ electroreduction activity at $E > -1.5$ V, making these potentials optimal for efficient EC via R-Hal activation with a minor contribution of competing CO₂ electroreduction.

4.2.2 Electrochemical reduction of benzylic halides

The voltammetric behavior of primary benzylic bromides **1a-c**, secondary benzylic bromides **2a,b**, benzyl chloride **3**, benzyl iodide **4**, and tertiary bromide **5** at different electrodes have been investigated by CV of 0.1 M solution of the bromide **1-5** in Ar-saturated CH₃CN containing 0.1 M TEABF₄ (Figures 4.3, 4.5, 4.6).

4.2.2.1 Benzyl bromide

The onset potentials of benzyl bromide **1a** reduction were highly dependent on the nature of the metal and ranged from -0.6 V to -1.6 V. The lowest onset potentials were observed for group 11 (Cu, Ag, Au) and group 10 (Pd, Pt) metals, as well as for Pb.

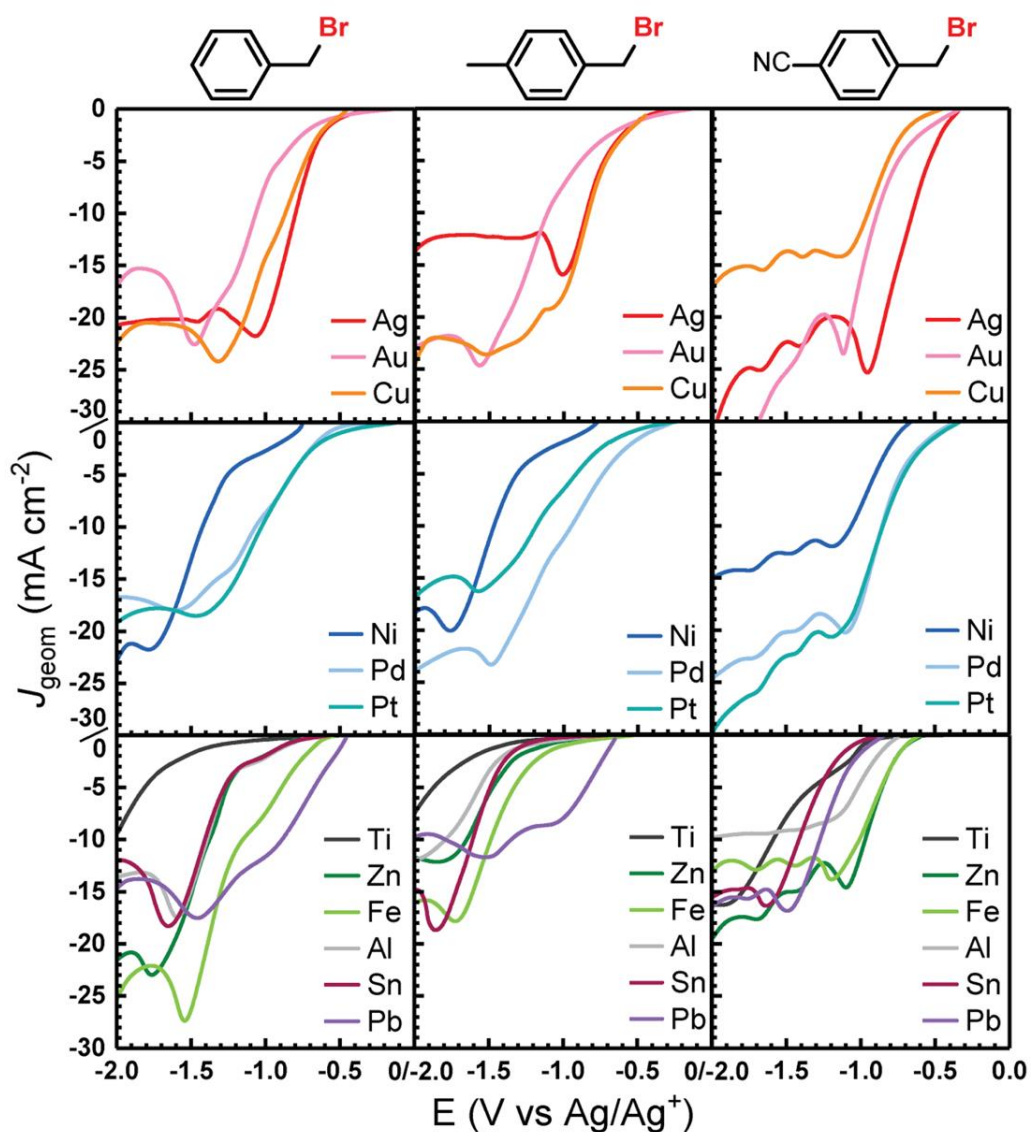


Figure 4. 3: Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of primary benzylic bromides **1a-c**. All voltammograms were recorded at 50 mV s⁻¹ scan rate at different bulk metal cathodes (working area ~ 0.2 cm²) in Ar-saturated CH₃CN containing 0.1 M TEABF₄. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

With the exception of Ti, all metal electrodes showed at least one reduction peak (Figure 4.3). Only in the case of Ag, two distinct peaks were observed in CV scans of bromide **1a**, which correspond to two major reduction processes: one-electron reductive cleavage of the C-Br bond with the formation of benzyl radical ($\text{PhCH}_2\text{Br} + 1\text{e}^- \rightarrow \text{PhCH}_2^\bullet + \text{Br}^-$; $E_p = -1.07$ V), and subsequent reduction of benzyl radical to the corresponding anion ($\text{PhCH}_2^\bullet + 1\text{e}^- \rightarrow \text{PhCH}_2^-$; $E_p = -1.45$ V). For Au, Cu, Pd, Pt and Pb, first reduction peak was observed as a shoulder of the second reduction peak, indicating that the reduction of $\text{PhCH}_2^\bullet$ to PhCH_2^- proceeds easier on these metals than on Ag and the two reduction steps are hardly separated from each other. For Ni, Fe, Zn, Al, and Sn only one reduction peak was observed at $E < -1.5$ V, more negative potentials than the reduction potential of $\text{PhCH}_2^\bullet$ ($E_{R^\bullet/R^-} = -1.43$ V vs SCE,²⁵⁹ or ~ -1.25 V vs Ag/Ag⁺). As benzyl radical has a less negative reduction potential than the parent molecule (PhCH_2Br), it is reduced instantly to corresponding anion at these metal electrodes and the overall process represent a stepwise two electron transfer ($\text{PhCH}_2\text{Br} + 1\text{e}^- \rightarrow \text{PhCH}_2^\bullet$ (slow) + $1\text{e}^- \rightarrow \text{PhCH}_2^-$ (fast)). Based on the position of the most pronounced reduction peak, metals can be ordered in terms of their activity towards **1a** reduction as follows: Ag > Cu > Pt, Au, Pd, Fe, Pb, Al > Ni, Sn, Zn > Ti.

4.2.2.2 4-Methylbenzyl bromide and 4-(bromomethyl)benzonitrile

To elucidate the effects of substituents on the electrochemical behavior of benzylic bromides at different metal electrodes, we performed a series of CV experiments for bromides with electron donating (EDG) methyl group **1b** and electron withdrawing (EWG) cyano group **1c** in the para position of the aromatic ring (Figure 4.3) compared to benzyl bromide **1a** with ΔE_{ons} of up to 0.4 V and ΔE_p of up to 0.2 V. Bromide **1b** bearing EDG showed negatively shifted onset and peak potentials for the majority of metals. This shift correlates with a more negative reduction potential of 4-Me-C₆H₄CH₂[•] ($E_{R^\bullet/R^-} = -1.62$ vs SCE,²⁵⁹ or ~ -1.44 V vs Ag/Ag⁺) compared to $\text{PhCH}_2^\bullet$. Similar to the reduction of **1a**, a single reduction peak was observed for Ni, Zn, Fe, Sn electrodes, indicating a stepwise two electron transfer. Ti and Sn did not show any reduction peaks. In the CV of Ag, Au, Cu, Pt, Pd, and Pb, two reduction waves were observed, either as two distinct peaks or as a peak and a shoulder. In contrast to all other metals, for Ag, the first reduction wave ($\text{R-Br} + 1\text{e}^- \rightarrow \text{R}^\bullet$) was more pronounced for both bromides **1a** and **1b** which indicates the better kinetics of the first electron transfer compared to the subsequent reduction of radical species. In the case of bromide **1c** with an EWG cyano group, a single irreversible peak followed by two

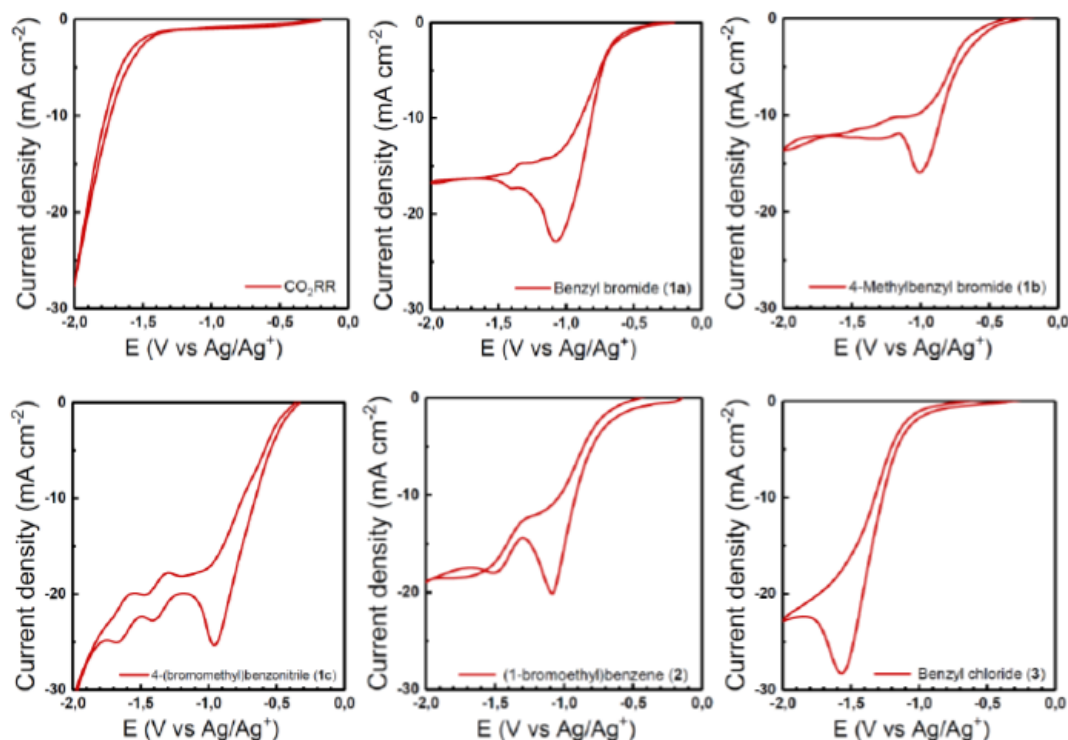


Figure 4. 4: Examples of CVs recorded for the reduction of CO₂ and benzyl halides 1-3 (100 mM) at Ag electrode. All voltammograms were recorded at 50 mV s⁻¹ scan rate in ACN containing 0.1 M TEABF₄. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

reversible peaks were observed for almost all studied metals (with the exception of Al and Ti; Figure 4.4). The first peak position was highly dependent on the nature of electrode material ranging from -0.96 V (Ag) to -1.63 V (Sn), while the positions of the following two peaks were consistent regardless of the nature of the metal (~ -1.4 V and -1.7 V, respectively). The first peak potential for all metals (at -1.0 V to -1.6 V) was more negative than the reduction potential of 4-CN-C₆H₄CH₂[•] ($E_{R^{\bullet}/R^-} = -0.77$ vs SCE,²⁵⁹ or ~ -0.6 V vs Ag/Ag⁺), and therefore this reduction wave can be attributed to the irreversible two-electron reduction of R-Br to R⁻. Thus, the electrochemical reduction of benzyl bromides bearing a strong EWG leads to the formation of highly unstable radical species that quickly undergo reduction to the corresponding anions. As the other two peaks at ~ -1.4 and ~ -1.7 V were not observed in the CVs of bromides **1a** and **1b**, this was a specific case for CN-substituted bromide **1c**. The observed reduction waves represent a reversible reduction of CN group in bromide **1c** and in electrochemically formed products (e.g., R-R, R-H) to N-centered radical anion.²⁶⁰

4.2.2.3 Secondary benzylic bromides: (1-bromoethyl)benzene and bromodiphenylmethane

The onset potentials for bromide **2a** were highly dependent on the metal and ranged from -0.55 V to -1.45 V (Figure 4.5). Two distinct reduction peaks were observed for Cu, Ag, Au, Ni, Pd, and Pt at potentials ranging from -1.05 to -1.2 V ($\text{Ph(Me)CH-Br} + 1\text{e}^- \rightarrow \text{Ph(Me)CH}^\bullet$) and -1.45 to -1.6 V ($\text{Ph(Me)CH}^\bullet + 1\text{e}^- \rightarrow \text{Ph(Me)CH}^-$). A good separation of waves corresponding to the one- and two-electron reduction processes on these metals is attributed to a higher stability of

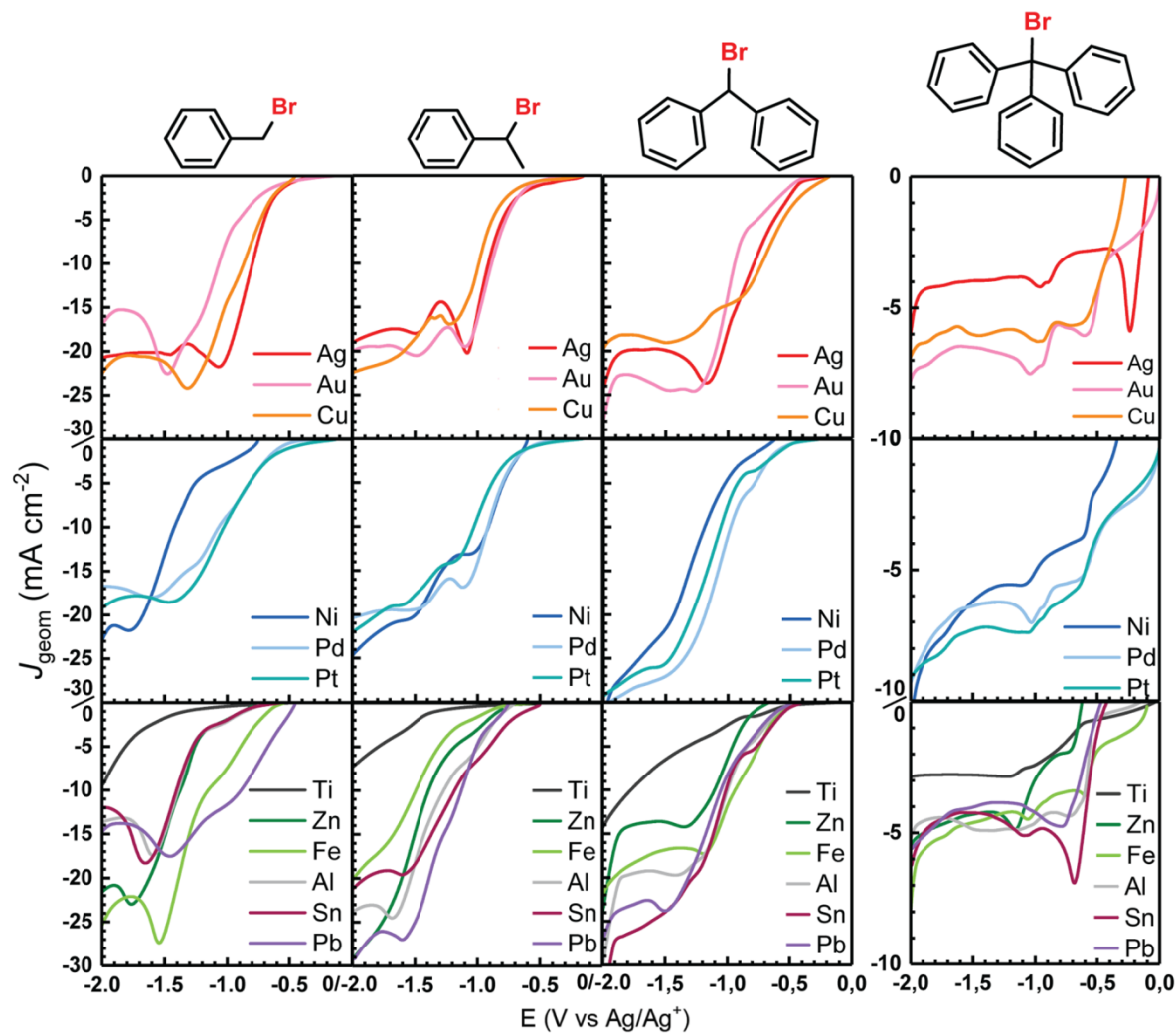


Figure 4. 5: Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of secondary benzylic bromides **2a,b** and 25 mM solution of tertiary benzylic bromide **5** (CVs for benzyl bromide **1a** are given for the reference). All voltammograms were recorded at 50 mV s⁻¹ scan rate at different bulk metal cathodes (working area ~ 0.2 cm²) in Ar-saturated ACN containing 0.1 M TEABF₄. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

a secondary radical compared to a primary radical derived from bromide **1a**. For Sn, Pb, and Al, an overlapping of the two reduction waves was observed. Fe, Zn and Ti did not show any reduction peaks. The onset potentials for bromide **2b** were observed at less negative potentials (-0.3 V to -0.8 V) than that for bromide **2a** (Figure 4.5). In contrast to **2a**, only Cu and Au showed two reduction waves for the reduction of **2b** ($\text{Ph}_2\text{CH-Br} + 1\text{e}^- \rightarrow \text{Ph}_2\text{CH}^\bullet$ at -0.9 V to -1.3 V; and $\text{Ph}_2\text{CH}^\bullet + 1\text{e}^- \rightarrow \text{Ph}_2\text{CH}^-$ at ~ -1.5 V). With the exception of Ti, other metals showed either peak with a shoulder (Ag, Pd, Pt, Sn, and Fe) or a single reduction peak (Ni, Zn, Al, and Pb). The observed trend indicates that a stepwise two-electron transfer is dominant for these metals, which is associated with lower energy requirements for the reduction of $\text{Ph}_2\text{CH}^\bullet$ compared to $\text{Ph(Me)CH}^\bullet$ (-0.9 V vs NHE and -1.49 V vs NHE, respectively).

4.2.2.4 Benzyl chloride and benzyl iodide

To show the effect of the halogen on the electrochemical behavior of benzyl halides, we performed a series of CV experiments for the reduction of benzyl chloride **3** and benzyl iodide **4** at different metal electrodes (Figure 4.6). The onset potentials for chloride **3** were observed at more negative potentials than for benzylic bromides **1a-c** and **2** (from -1.0 V to -1.5 V vs Ag/Ag^+), which correlates with a higher bond dissociation energy of C-Cl bond compared with C-Br for benzyl halides ($\sim 300 \text{ kJ mol}^{-1}$ and 257 kJ mol^{-1} , respectively).²⁶¹ In contrast to benzyl bromide **1a**, only single peaks were observed for Ag, Au, Cu, Pd, Pt and Pb (from -1.55 V to -1.8 V vs Ag/Ag^+) and no peaks were observed for other metals. As the reduction peaks were observed at more negative potentials than the reduction potential of $\text{PhCH}_2^\bullet$, thus, the overall process can be considered a two-electron reduction leading to PhCH_2^- . The onset potentials for iodide **4** were observed at less negative potentials (-0.2 V to -1.4 V) than that for benzyl chloride and bromide (Figure 4.6). The lower energy requirements for the reduction of iodide **4** is associated with relatively low dissociation energy of C-I bond (188 kJ mol^{-1})²⁶¹. Two distinct reduction peaks were observed for Ag, Au, and Pb, indicating better separation of first and second reduction processes compared to benzyl bromide. Thus, benzyl iodide is a better organic substrate for the generation of radical species rather than anions. Ag, Ni, Pd, Pt, Pb and Zn showed peak and a shoulder, while Sn, Al, Fe, and Ti did not show any distinct peaks.

4.2.2.5 Bromotriphenylmethane

Finally, the reduction of tertiary bromide **5** has been studied. In contrast to primary and secondary benzylic halides **1-4**, bromide **5** spontaneously dissociates giving a rise to cation Ph_3C^+ , thus, a completely different reduction mechanism is expected in this case. With the exceptions of Ti and Pb, all metals showed two reduction waves that correspond to the cation reduction to the

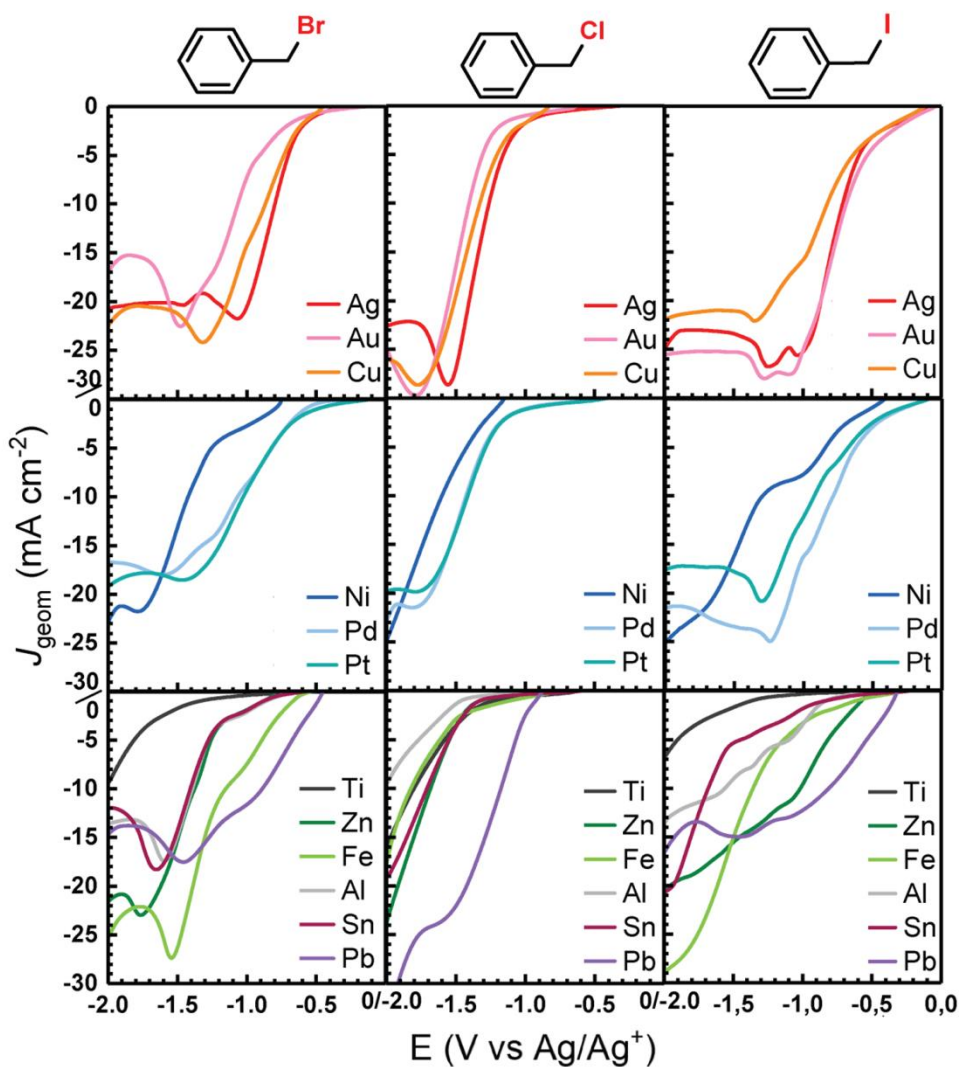


Figure 4. 6: Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of benzyl chloride **3** and benzyl iodide **4** (CVs for benzyl bromide **1a** are given for the reference). All voltammograms were recorded at 50 mV s^{-1} scan rate at different bulk metal cathodes (working area $\sim 0.2 \text{ cm}^2$) in Ar-saturated CH_3CN containing 0.1 M TEABF_4 . Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

radical ($\text{Ph}_3\text{C}^+ \rightarrow \text{Ph}_3\text{C}^\bullet$ at -0.24 V to -0.7 V), and radical reduction to the anion ($\text{Ph}_3\text{C}^\bullet \rightarrow \text{Ph}_3\text{C}^-$ at -1.0 V to -1.3 V). For Pb, only the first reduction peak at -0.8 V was observed, while Ti did not show any distinct peaks.

4.2.3 Electrochemical reduction of benzylic halides at carbon-based electrodes

To elucidate the catalytic activity of metals towards electrochemical reduction of organic halides, we compared the voltammetric behavior of the halides **1-5** at different metal electrodes to that at a glassy carbon electrode (Figure 4.7a). The reduction of benzyl bromide **1a** at GC was observed at $E < -1.2$ V with a peak at -1.75 V. With the exception of Ti, all metals showed less negative onset potentials. The catalytic activity of metal electrodes was quantified by $\Delta E_p = E_p(\text{M}) - E_p(\text{glassy carbon})$,²⁶² where $E_p(\text{M})$ and $E_p(\text{glassy carbon})$ represent peak potentials for metal electrode and for glassy carbon, respectively. The value of ΔE_p ranged from 0.68 V to -0.42 V. Based on ΔE_p value, metals can be ordered in terms of their catalytic activity towards **1a** reduction as follows: Ag (0.68 V) > Cu (0.42 V) > Pt, Au, Pb (0.26 ÷ 0.3 V) > Fe, Pd, Al (0.14 ÷ 0.21 V) > Sn (0.09 V) > Zn, Ni (-0.04 ÷ -0.02 V) > Ti (-0.42 V). A remarkable catalytic activity was observed for Ag as well as for Cu, Pt, Au and Pb. Fe, Pd and Al showed a moderate catalytic activity towards the reduction of **1a**, while Sn, Zn, Ni and Ti did not show any enhanced activity compared to glassy carbon. Moreover, the negative ΔE_p value of -0.42 V observed for Ti indicated its poor

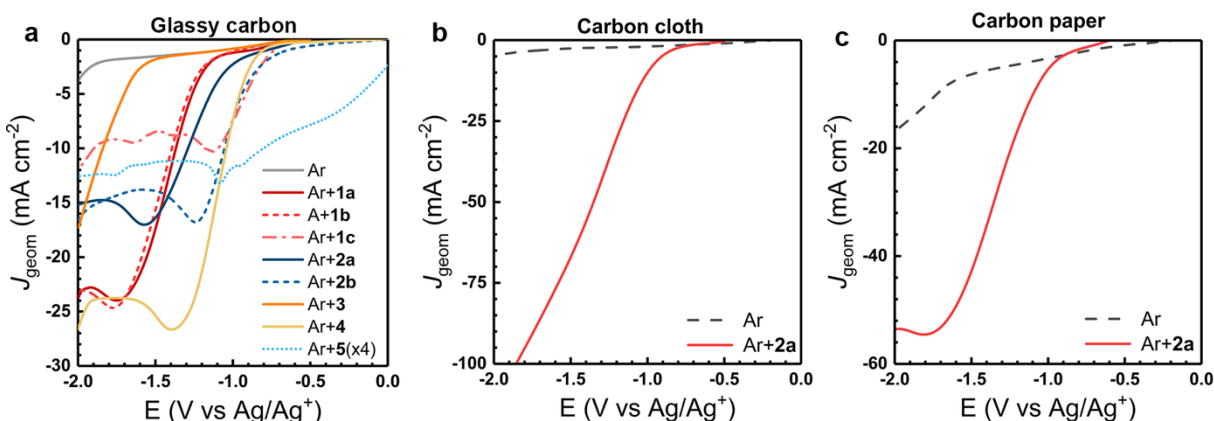


Figure 4. 7: Cathodic sweeps of CVs recorded for the reduction of 100 mM solutions of benzylic halides **1a-c** (a), **2a** (a-c), **2b** (a) and **3-5** (a). Voltammograms were recorded at 50 mV s⁻¹ scan rate at glassy carbon (a), carbon cloth (b) and carbon paper (c) (working area ~ 0.1 cm²) in Ar-saturated CH₃CN containing 0.1 M TEABF₄. Dashed lines for carbon cloth and carbon paper correspond to the electrochemical behavior of cathodes in the absence of substrate. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

electrochemical activity. Due to the absence of catalytic activity in case of Sn, Zn, Ni and Ti, one can assume that the reduction of **1a** on these metals proceeds via the outer sphere electron transfer.

The reduction of benzylic bromide **1b** with EDG at glassy carbon was observed at $E < -1.2$ V with a peak at -1.78 V, i.e., at a more negative potential than unsubstituted benzyl bromide. A significant positive shift of the onset (to -0.72 V) and peak potential (to -1.14 V) with respect to the unsubstituted benzyl bromide was observed in the case of benzylic bromide **1c** with EWG. A noticeable catalytic activity towards the reduction of **1b** with ΔE_p values of $0.23 \div 0.78$ V was observed for Ag, Pb, Pt, Pd, Au and Cu, while the other metals behaved as non-catalytic electrodes. A positive shift of the peak potential for **1c** reduction was observed only in the case of Ag (~ 0.21 V), indicating that the reduction on other metals likely proceeds via the outer sphere electron transfer. Similar to the metal electrodes, additional two peaks at ~ -1.4 V and ~ -1.6 V related to the reduction of CN group were observed in the CV of **1c** at glassy carbon. Since the position of these peaks was the same regardless of the electrode nature, this reduction process should also proceed *via* the outer sphere electron transfer.

The reduction of a secondary bromide **2a** at glassy carbon was observed at $E < -1$ V with a peak at -1.58 V. The presence of catalytic activity in this case was observed for group 10 and 11 metals (Cu, Ag, Au, Ni, Pd, Pt) with ΔE_p values of $0.34 \div 0.51$ V. Interestingly, Ni showed an enhanced activity towards the reduction of bromide **2a** in contrast to the reduction of primary bromides **1a-c**. A positive shift of both onset and peak potentials was observed for the reduction of secondary bromide **2b** at glassy carbon (to -0.7 V, and to -1.24 V, respectively) compared to that for bromide **2a**. Noticeable catalytic activity was observed only for Cu and Ag with ΔE_p values of $0.38 \div 0.12$. Interestingly, in the case of tertiary bromide **5**, all metals showed high catalytic activity with ΔE_p values of $0.3 \div 0.9$ V.

The reduction of benzyl chloride **3** at glassy carbon was observed at $E < -1.5$ V with no peak in the studied range of potentials. Ag, Au, Cu, Ni, Pd, Pt and Pb showed less negative onset potentials for the reduction of **3**, while other metals did not show a significant difference in the onset potentials compared to glassy carbon. The reduction of benzyl iodide at glassy carbon was observed at $E < 0.8$ V with a reduction peak at -1.39 V. Ag, Au, and Pb showed highest catalytic activity with ΔE_p values of up to 0.4 V. Other metals showed only moderate to no catalytic activity.

In addition, we performed a series of CV experiments for the reduction of bromide **2a** at some other typical carbon support materials (carbon paper and carbon cloth; Figure 4.7b,c). In the

absence of an organic substrate (Ar-saturated 0.1 M TEABF₄) carbon paper showed noticeable currents at $E < -1.6$ V, indicating a significant activity of the surface in the aprotic media, while carbon cloth along with glassy carbon were inactive. The electrochemical activity of carbon paper in the absence of any organic substrates can be associated with the presence of hydrophobic additives, such as Teflon, which may participate in electroreductive transformations.²⁶³ In the presence of **2a**, both carbon-based supports were active towards the reduction of benzylic bromide **2a** at $E < -0.8$ V, with performance comparable to that of glassy carbon; we note that no peak was observed in the CV in the case of carbon cloth, likely due to mass transport limitations associated with a high surface area of this material.

4.2.4 Electrochemical reduction of benzylic bromides in the presence of CO₂

As mentioned above, the reduction of benzylic bromides in the presence of CO₂ yields carboxylate ($\text{RBr} + \text{CO}_2 + 2\text{e}^- \rightarrow \text{RCO}_2^- + \text{Br}^-$). EC can proceed either via the activation of R-Hal or via the activation of CO₂ yielding the same product. The mechanism of EC in the potential window of CO₂ stability ($E > -1.5$ V) is well understood and represents a nucleophilic addition of electrogenerated carbanions to CO₂. At more negative potentials, the mechanism becomes more complex due to the formation of $\text{CO}_2^{\bullet-}$. To elucidate the effect of the presence CO₂ on EC, we

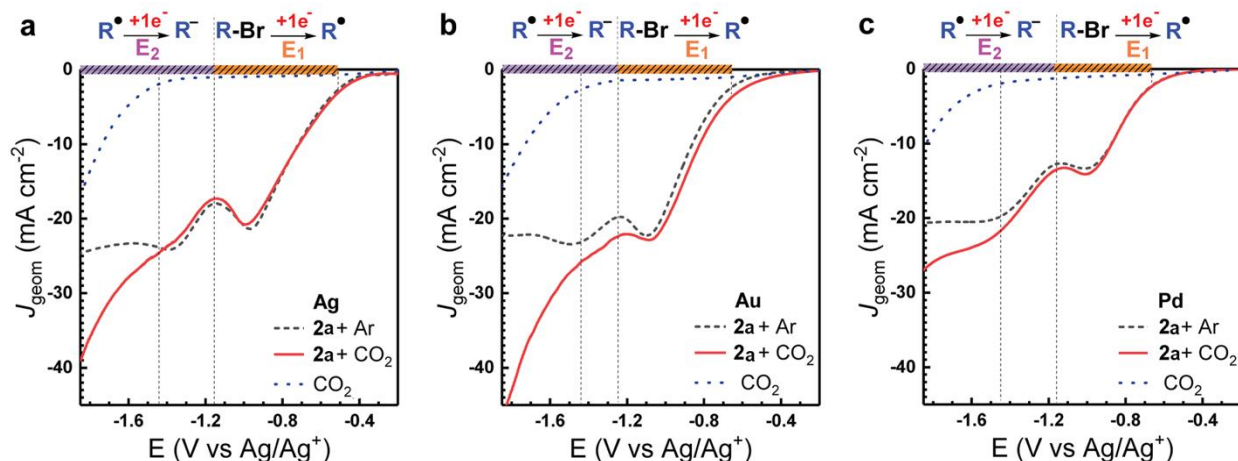


Figure 4. 8: Cathodic sweeps of CVs recorded for the reduction of 100 mM solutions of (1-bromoethyl)benzene **2a**. Voltammograms were recorded at 50 mV s⁻¹ scan rate at Ag-, Au- and Pd-foil cathodes (working area ~ 0.2 cm²) in CO₂-saturated (solid red trace) and Ar-saturated (dashed black trace) CH₃CN containing 0.1 M TEABF₄. CVs for the reduction of CO₂ (dotted blue trace) are shown for reference. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

carried out a series of CV experiments for the reduction of bromide **2a** in Ar- and CO₂-saturated electrolyte (0.1 M TEABF₄) at Ag, Au and Pd electrodes (Figure 4.8). The organic substrate and the electrodes were chosen due to a high distance between two reduction peaks in these systems ($\Delta E = 370 \div 440$ mV) that makes possible to separately analyze the effect of CO₂ on the electrochemical conversion of **2a** to the corresponding radical and anion.

The CV curves for the reduction of bromide **2a** were almost identical for Ar- and CO₂-saturated electrolyte in the radical zone for all three metals, which supports the absence of interactions between R[•] species and CO₂. Noticeable changes in CV curves were observed at more negative potentials after CO₂ electroreduction onset potential: the reduction currents were significantly increased in the presence of CO₂ (in 1.6, 2.0 and 1.4 times at -1.8 V for Ag, Au, and Pd, respectively). These changes indicate the presence of a new reduction process besides the reduction of bromide **2a**, i.e. $\text{CO}_2 + 1\text{e}^- \rightarrow \text{CO}_2^{\bullet-}$. In our previous studies, we showed that at these potentials, CO was not formed in a course of EC of **2a** at Ag electrode when the concentration of an organic substrate was relatively high (0.05 M); however, the formation of CO was observed, when the concentration was low.⁷⁶ The higher current densities observed in EC and the absence of CO as a product support the hypothesis that $\text{CO}_2^{\bullet-}$ reacts with R-Br yielding carboxylate. One of the possible mechanisms is the electron transfer from $\text{CO}_2^{\bullet-}$ to R-Br²⁶⁴ leading to R[•] and its subsequent coupling with excess of $\text{CO}_2^{\bullet-}$. A detailed understanding of the interactions of reactive intermediates of both EC and CO₂ electroreduction with the catalytic surface is required for a better description of the reaction mechanism at high negative potentials. However, these interactions are rarely considered in the electrochemical reduction of organic halides²⁶⁵, especially in EC⁷⁶.

In all studied combinations of the organic substrates and electrode materials, no to minor influence of CO₂ on the electrochemical behavior of bromide **2a** was observed in the CO₂ electrochemical window. At more negative potentials, the presence of both EC mechanisms, via the activation of R-Hal and *via* the activation of CO₂, is expected due to a limited mass transport of both CO₂ and R-Hal species to the electrode surface. The contribution of the latter mechanism for a specific metal electrode should correlate with the rate of CO₂ electroreduction at that metal (Figure 4.2). Thus, based on our experimental data presented in the Section 3.1, at $E < -1.5$ V, the highest rates of EC *via* CO₂ activation are expected for Ag and Au, followed by Cu, Pt and Pd.

In addition to the CV studies, we performed potentiostatic electrolysis of benzyl bromide **1a** in the presence of CO₂. All reactions were carried out at the initial bromide concentration of 25

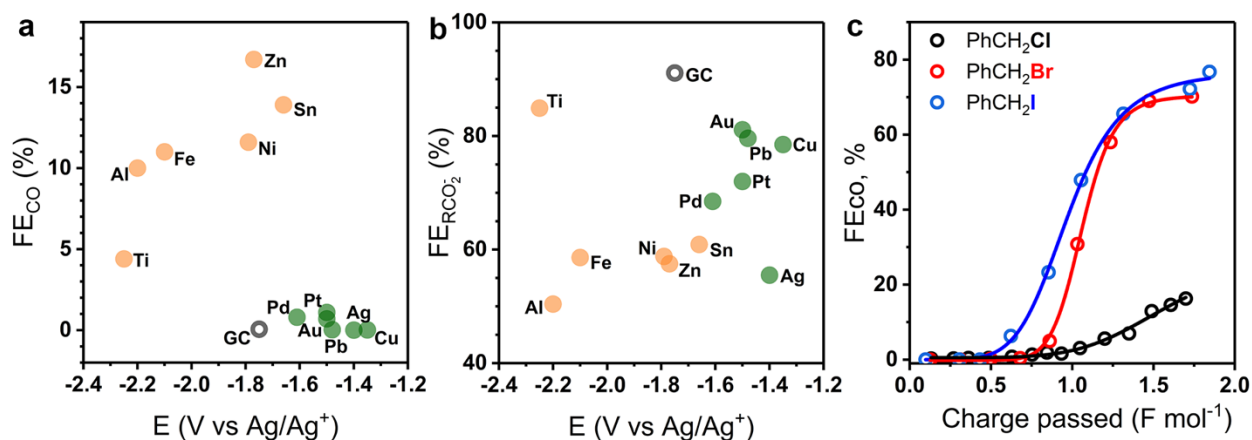


Figure 4. 9: Total Faradaic efficiencies of CO (a) and carboxylate (b) in the electrolysis of 25 mM benzyl bromide + CO₂-saturated CH₃CN–0.1 M TBABr₄ as a function of applied potential and the electrode nature. Green circles correspond to the electrodes favoring EC with minor contribution of competing CO₂ electroreduction. (c) Faradaic efficiencies of CO in the electrolysis of 25 mM benzyl bromide, chloride, and iodide performed at -1.9 V as a function of charge passed. GC corresponds to glassy carbon electrode in this figure. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

mM using different metals and glassy carbon as cathodes. With a few exceptions, the potentials for electrolysis were selected near the reduction peak in the cathodic sweeps of the CV that correspond to 2e⁻ transfer. Electrolysis was performed at more negative potentials in case of Al and Fe due to the low activity of these electrodes at peak potentials under the electrolysis conditions. All reactions were stopped after passing electric charge of 1 F mol⁻¹. The gas products were analyzed using the in-line GC analysis every 20 minutes that allowed us to estimate FE_{co}(t) dependence and calculate total FE of CO. The products of benzyl bromide reduction were analyzed and quantified by NMR of crude reaction mixture with 1,2,4,5-tetrachlorobenzene as an internal standard. The results are summarized on the Figure 4.9a,b. The major products of all reactions were carboxylate RCO₂⁻ with FEs ranging from 50 to 91%, dimer R-R (0-36%), and CO (0-17%). Cu, Ag, Au, Pd, Pt, Pb, and GC showed the lowest FEs of CO, since the carboxylation reactions proceeded at the potentials near the CO₂ electroreduction onset. The FE of carboxylate was high for all electrodes but Ag. In the case of Ag, the main by-product was R-R (36%) that was formed by the coupling of electrogenerated radicals. From all the aforementioned metal electrodes, Cu and Au showed the highest FE of carboxylate (up to 81%). Other tested metals (Ni, Zn, Fe, Al, Sn)

showed noticeable FEs of CO and only moderate FEs of carboxylate. Ti was the only exception, and FE of CO in this case was only 4.4% even though the applied potential was very negative (-2.25 V). The FE of carboxylate was also surprisingly high in this case (~85%). Overall, the highest FEs of carboxylate were observed for three catalytic metals (Cu, Au, and Pb; $\text{FE}_{\text{RCO}_2^-} \sim 80\%$) and two non-catalytic electrodes (Ti and glassy carbon; $\text{FE}_{\text{RCO}_2^-}$ of up to 91%). Even though the highest FE of carboxylate were observed at non-catalytic electrodes, the reaction in these cases proceeded at more negative applied potentials compared to Cu, Au and Pb.

Finally, to show the effect of the halogen on the competition between EC and CO_2 electroreduction processes, we performed potentiostatic electrolyses of benzyl bromide, chloride and iodide at Ag electrode at high negative applied potential of -1.9 V corresponding to the two-electron reduction peak (Figure 4.9c). In all these cases, almost no CO was produced in the beginning of the electrolysis ($Q < 0.5 \text{ F mol}^{-1}$). Noticeable FEs of CO ($> 2\%$) were observed for electrolysis benzyl iodide, bromide, and chloride after passing an electrical charge of 0.5, 0.75 and 0.1 F mol^{-1} , respectively. FE of CO in the case of the bromide and iodide raised to 80% close to 2 F mol^{-1} charge passed, while in the case of the chloride FE of CO was still below 20%. The difference between the halides behavior at high negative potentials can be associated with their different adsorption profiles. For instance, it was shown that binding of benzylic bromides to the Ag surface decreases with a shift of applied potentials to more negative values.⁷⁶

4.2.5 Summary of the results

Figure 4.10 summarizes the performance of all studied metal electrodes towards the reduction of benzylic halides **1-4** and CO_2 . Metals in group 11 (Cu, Ag, Au) and group 10 (Pd, Pt; also Ni for halide **2** only), as well as Pb in some cases (for halides **1a,b**) showed the highest activities in both electroreduction processes making these metals the most promising materials for electrochemical reduction of organic halides. Due to the enhanced catalytic activity observed for these metals, it is expected that the atomic and nanoscale surface morphology can significantly affect efficiency and selectivity of EC, as it has been shown for other electrocatalytic processes.^{266,267} Systematic studies of nanostructured electrodes comprised of these metals in EC is a promising route to further optimization of the onset potentials and the activity of the electrocatalytically active sites. Zn, Fe, Sn and Al showed moderate to low activity in the majority

of studied reduction processes; Ti was found to be inefficient towards EC. Moreover, the latter metals did not show noticeable catalytic activity.

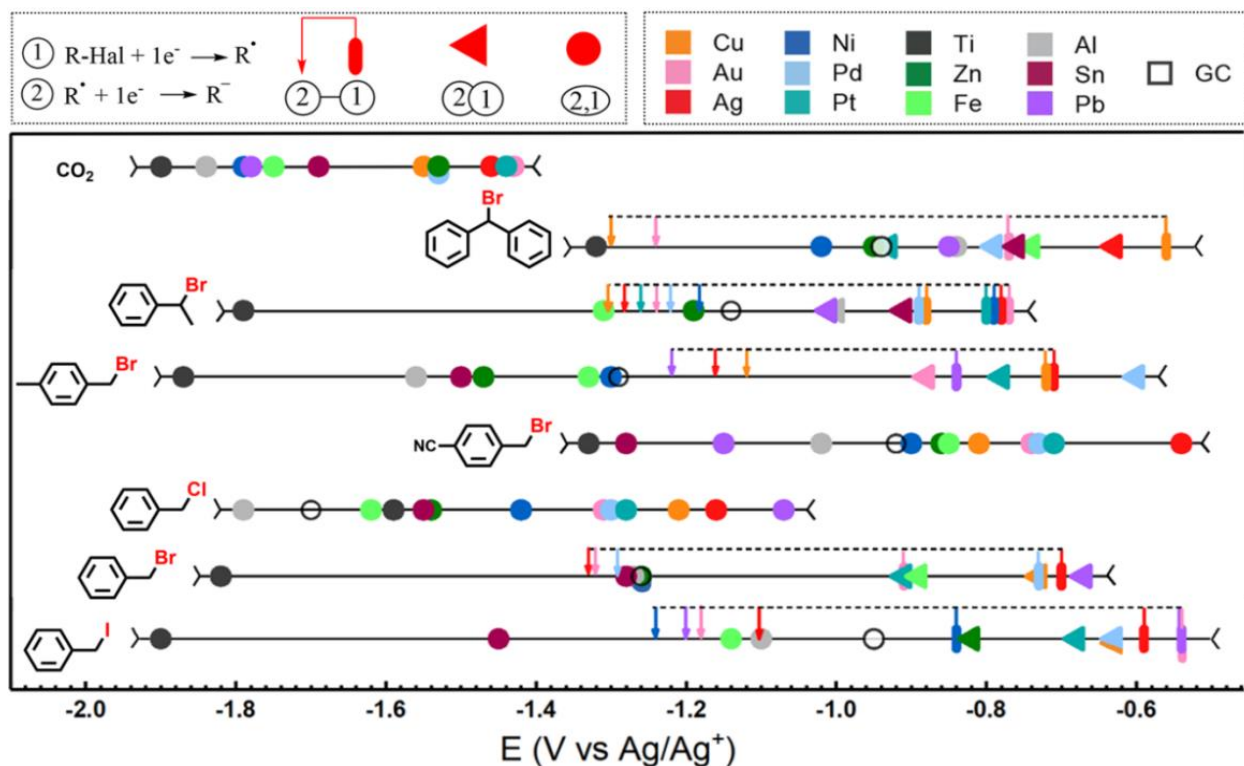


Figure 4. 10: The potentials of the electrochemical reduction of organic halides **1-4** and CO_2 at different bulk metal cathodes in CH_3CN containing 0.1 M TEABF_4 . The pin colors correspond to cathode materials (see the legend on the top). The empty circles correspond to the potentials at 5 mA cm^{-2} for the two-electron reduction of R-Hal at glassy carbon. The filled bars correspond to the potentials at 5 mA cm^{-2} for the one-electron reduction of benzylic halides ($\text{R-Hal} + 1\text{e}^- \rightarrow \text{R}^\bullet$) for the cases when two separate reduction waves are observed in CV; the downward arrows correspond to the onset potentials of the second reduction wave, $\text{R}^\bullet + 1\text{e}^- \rightarrow \text{R}^-$. The triangles correspond to the potentials at 5 mA cm^{-2} for the one-electron reduction of benzylic halides for the cases when two reduction waves are overlapped. The filled circles correspond to the potentials at 5 mA cm^{-2} for the two-electron reduction of R-Hal to R^- for the cases when a single peak is observed. In the case of CO_2 electroreduction, the circles correspond to the onset potentials of the reduction CO_2 to $\text{CO}_2^{\bullet-}$. Reprinted with permission from ref. [280]. Copyright 2021, Elsevier.

The mechanism of R-Hal reduction was found to be highly dependent on both the nature of the electrocatalyst and the structure of the organic substrate. With the exception of organic

halides bearing a strong EWG, the first electron transfer proceeds at relatively low potentials ($E < -0.6$ V); however, the second electron transfer ($R^{\bullet} + 1e^- \rightarrow R^-$) requires a higher energy input and generally proceeds at $E < -1.1$ V for all studied metal electrodes. The presence of EWG in the structure of a halide significantly lowers the energy requirements for the second electron transfer, which in this case can proceed at $E > -1.0$ V. The EC of organic halides via the activation of R-Hal occurs in a narrow potential window ($\Delta E \sim 0.1 \div 0.7$ V for halides **1a,b**, **2** and **3**; $\sim 0.4 \div 0.9$ V for halide **1c**). Among the metals with high catalytic activity towards the reduction of organic halides, Ni and Pb showed the widest gap between EC and CO₂ electroreduction with $\Delta E > 0.5$ V, while for other catalytic metals ΔE ranged from 0.1 to 0.3 V. At high negative potentials the competing formation of CO₂^{•-} species is observed. Even though at high concentrations of organic substrate the CO₂^{•-} species still participate in EC, with a decrease in the organic substrate concentration competing CO₂ electroreduction starts to dominate, resulting in decreased faradic efficiencies of EC. Subsequently, this factor can lead to difficulties in achieving full conversion without CO as a side product. Metal nanoparticles with optimized catalytic sites can solve the problem with a narrow potential gap between CO₂ electroreduction and EC by selectively decreasing the energy requirements for the second electron transfer ($R^{\bullet} + 1e^- \rightarrow R^-$). Moreover, the absence of the direct correlation between the activity of a metal towards the reduction of an organic halide and CO₂ makes possible further EC optimization by favoring the electrocatalyst selectively towards reducing an organohalide in the presence of CO₂ in a wide potential range while avoiding CO₂ activation. Nanoparticle-based electrodes typically rely on a conductive carbon support for electrode fabrication, but due to the intrinsic activity of several commercially available bare supports under EC reaction conditions (Figure 4.7) the surface of the support should be well covered by nanoparticles to exclude its effect on the electroreduction process. Alternatively, conductive metals such as Ti with low activity towards EC and CO₂ electroreduction can be used as supports.

4.3 Electrocarboxylation of imines

The significant effect of electrocatalyst nature on the outcome of EC of organohalides inspired us to screen various metal cathodes towards the EC of other classes of organic compounds. Imines were of great interest as their EC leads to amino acids and only a few studies were performed on this topic even with sacrificial metal anodes.²⁶⁸⁻²⁷⁴

In analogy with EC of organohalides, we studied a sacrificial anode-free approach for the EC of imines in a divided cell. Specifically, we explored the EC of N-benzylideneaniline in ACN paired with bromide oxidation at the anode (Figure 4.11a). The arbitrary anodic reaction was the oxidation of electrolyte (Br^- from TBABr) that, as was demonstrated in Chapter 3, can be replaced by OER, UOR, or AOR. To elucidate the effect of the cathode material on the reaction outcome, we summarized the performance of 10 bulk metal cathodes (Ti, Zn, Au, Pd, Pt, Sn, Ag, Ni, Fe, Cu) and glassy carbon.

4.3.1 Screening of bulk electrodes for the reductive activation of N-benzylideneaniline and CO_2

Similarly to organohalides, the EC of imines can proceed *via* two different mechanisms.²⁷⁵ The reaction can occur either *via* the activation of imine or *via* the activation of CO_2 yielding the same radical-anion intermediate $\text{PhCH}(\text{CO}_2^-)\text{-PhN}^\bullet$, which then undergoes further reduction to α -amino acid (α -AA) (Figure 4.11b).²⁷⁵ It should be noted that the active reaction intermediates, i.e., $\text{PhCH}^-\text{-PhN}^\bullet$ and $\text{CO}_2^{\bullet-}$, can be also involved in side reactions: hydrogenation^{275,276} or CO_2 reduction to CO or oxalate.²⁷⁷ Both processes are not desirable as they significantly decrease the

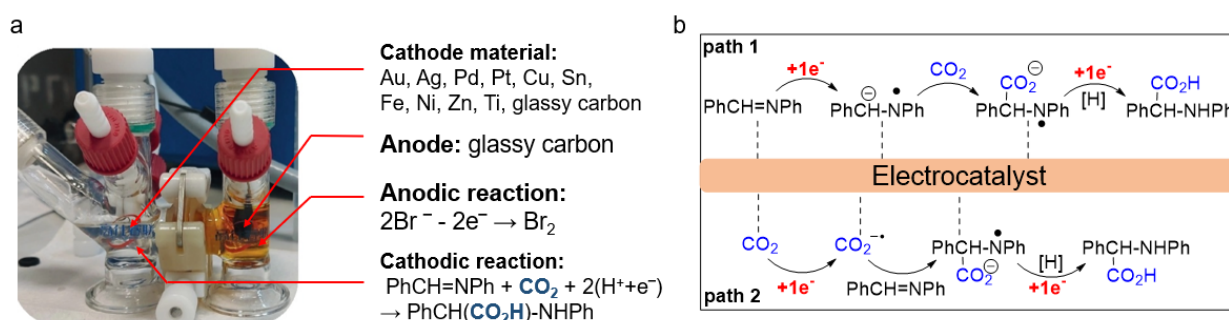


Figure 4. 11: (a) The photo of the electrochemical cell used for the electrosynthesis of α -amino acids *via* electrocarboxylation of imines, comprising cathode, anode, and reference electrode; cathodic and anodic compartments are separated by an anion exchange membrane. (b) Two mechanisms proposed in the literature for the electrochemical carboxylation of imines.

FE of target α -AA. Since the nature of the electrocatalyst affects the energies of intermediates involved in a process, an appropriate choice of the catalyst can improve the selectivity of EC.

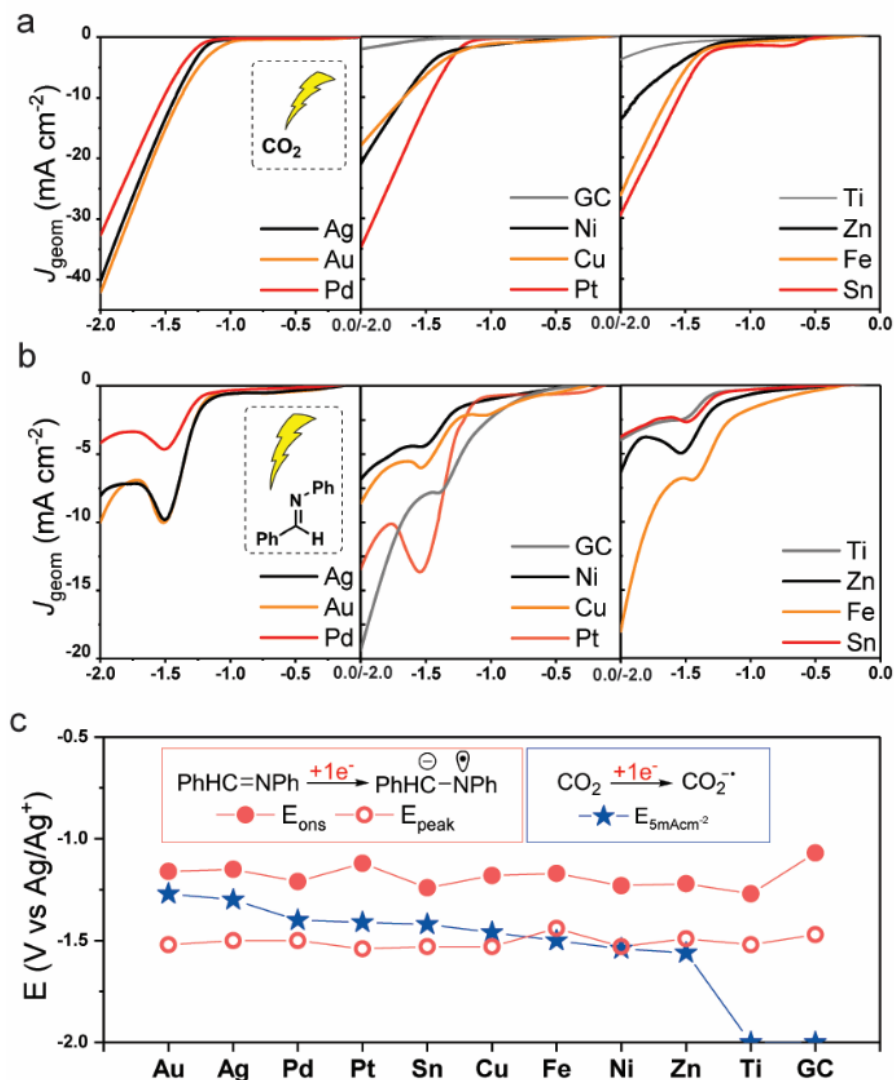


Figure 4. 12: The electrochemical behaviour of CO_2 and N-benzylideneaniline at different catalyst surfaces. (a,b) Cathodic sweeps of CV recorded for the reduction of CO_2 (a) and the reduction of 25 mM N-benzylideneaniline. All CVs were recorded at 100 mV s^{-1} scan rate at different bulk metal and glassy carbon cathodes in (a) CO_2 -saturated or (b) Ar-saturated CH_3CN containing 0.1 M TEABF $_4$. (c) The comparison of the potentials of the electrochemical reduction of N-benzylideneaniline and CO_2 at different bulk metal cathodes in CH_3CN containing 0.1 M TEABF $_4$. GC corresponds to glassy carbon in this figure.

To compare the energy requirements for each pathway, we investigated the electrochemical behavior of CO₂ and *N*-benzylideneaniline at different bulk metal cathodes and glassy carbon in an inert electrolyte (0.1 M TEABF₄ + ACN). First, we investigated the electrochemical behavior of CO₂ by performing CV in the CO₂-saturated electrolyte (Figure 4.12a). The noticeable activity (5 mA cm⁻²) of catalysts towards CO₂ electroreduction ranged from about -1.3 V to -2 V depending on the catalyst nature. The highest activity was observed for noble metals (Au, Ag, Pt, and Pd: up to 42 mA cm⁻² at -2 V) followed by Sn, Fe, Cu, Ni, and Zn (13-29 mA cm⁻² at -2 V) with moderate activity. Glassy carbon and Ti cathodes did not show any noticeable CO₂ electroreduction activity in the studied potential region. Second, the electrochemical behavior of the imine was studied in Ar-saturated electrolyte (Figure 4.12b). In contrast to CO₂, the onset potentials of the imine reduction were not highly dependent on the nature of the metal and ranged from -1 V to -1.2 V. All metal electrodes showed one reduction peak, which corresponds to the first electron transfer ($\text{PhCH=NPh} + 1\text{e}^- \rightarrow \text{PhCH}^-\text{--PhN}^\bullet$).⁴² As the reduction peak potentials were almost independent of the catalyst nature, the reduction can be approximated as an outer-sphere electron transfer, indicating the absence of a strong interaction between the imine and the catalyst surface. Notably, at high negative potentials (-2 V), the imine reduction current densities were generally much lower than that for CO₂ reduction: up to 20 mA cm⁻² and up to 42 mA cm⁻², respectively. Aforementioned observations along with the comparison of the potentials required for CO₂ electroreduction and EC (Figure 4.12c) allowed us to make the following conclusions: (1) the activation of imines proceeds at less negative potentials than that for CO₂; (2) both EC mechanisms can occur at the EC peak potential (about -1.5 V), but the contribution of the mechanism through CO₂ activation appears to be minor; (3) at more negative potentials the mechanism through CO₂ activation is likely dominant.

4.3.2 Electrochemical reduction of *N*-benzylideneaniline in the presence of CO₂: product distribution

To elucidate the effect of the catalyst nature on the EC product distribution, we performed potentiostatic electrolysis of *N*-benzylideneaniline in the presence of CO₂. All reactions were performed in a divided cell at the initial imine concentration of 25 mM using different metals and glassy carbon as cathodes. For the electrolyses, we applied EC peak potentials corresponding to the highest EC current densities observed in the cathodic sweeps of CV. All reactions were stopped after passing a charge of 1 F mol⁻¹ that corresponds to the charge required for 50% imine conversion. The gas products were analyzed using the in-line gas chromatography, which allowed

us to calculate the total FE of CO. The products of imine EC were determined and quantified by the thin-layer chromatography (TLC) and NMR.

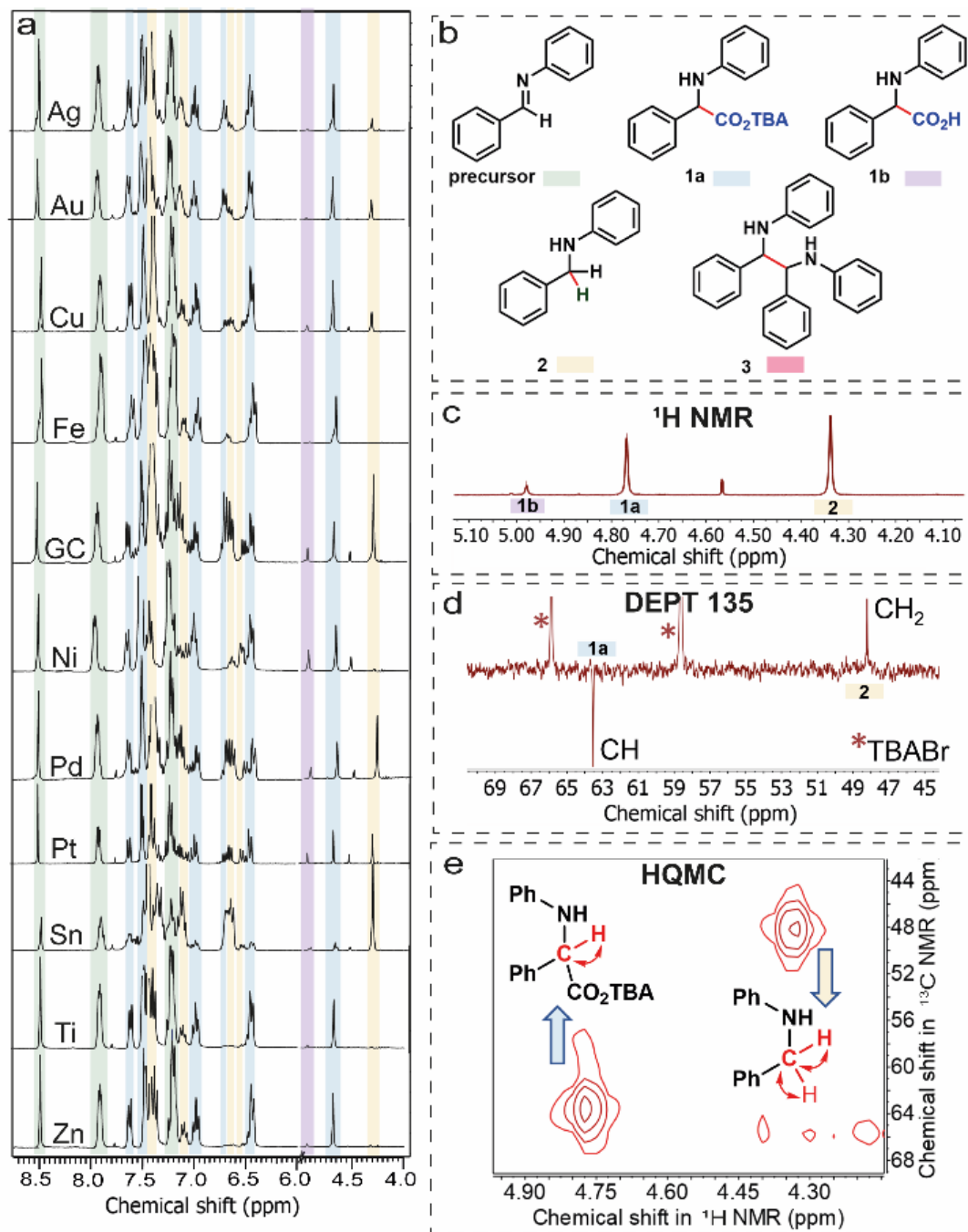


Figure 4. 13: The identification of major reaction products. (a) NMR spectra of the crude reaction mixtures after the EC of N-benzylideneaniline using different cathodes. (b) The structures of organic precursor and expected products of the electrolysis. (c-e) ^1H NMR, DEPT 135, and HQMS spectra recorded for the crude reaction mixture.

First, to identify the number of the major reaction products, the TLC of crude reaction mixtures was carried out (mobile phase hexane:acetone 4:1). The TLC analysis demonstrated the formation of at least two major products in addition to the unreacted imine. Next, the NMR analysis of crude reaction mixture was performed. ^1H NMR spectra of all reaction mixtures contained three new characteristic signals at 4.3 ppm, 4.77 ppm, and 5.0 ppm (Figure 4.13a,b). DEPT 135 and HMQC NMR spectra (Figure 4.13c,d) showed that the peak at 4.77 ppm corresponds to CH group, while the peak at 4.3 ppm corresponds to CH_2 group. Based on the proposed reaction mechanism and the reported in the literature NMR spectra for possible EC products,^{278,279} these two peaks

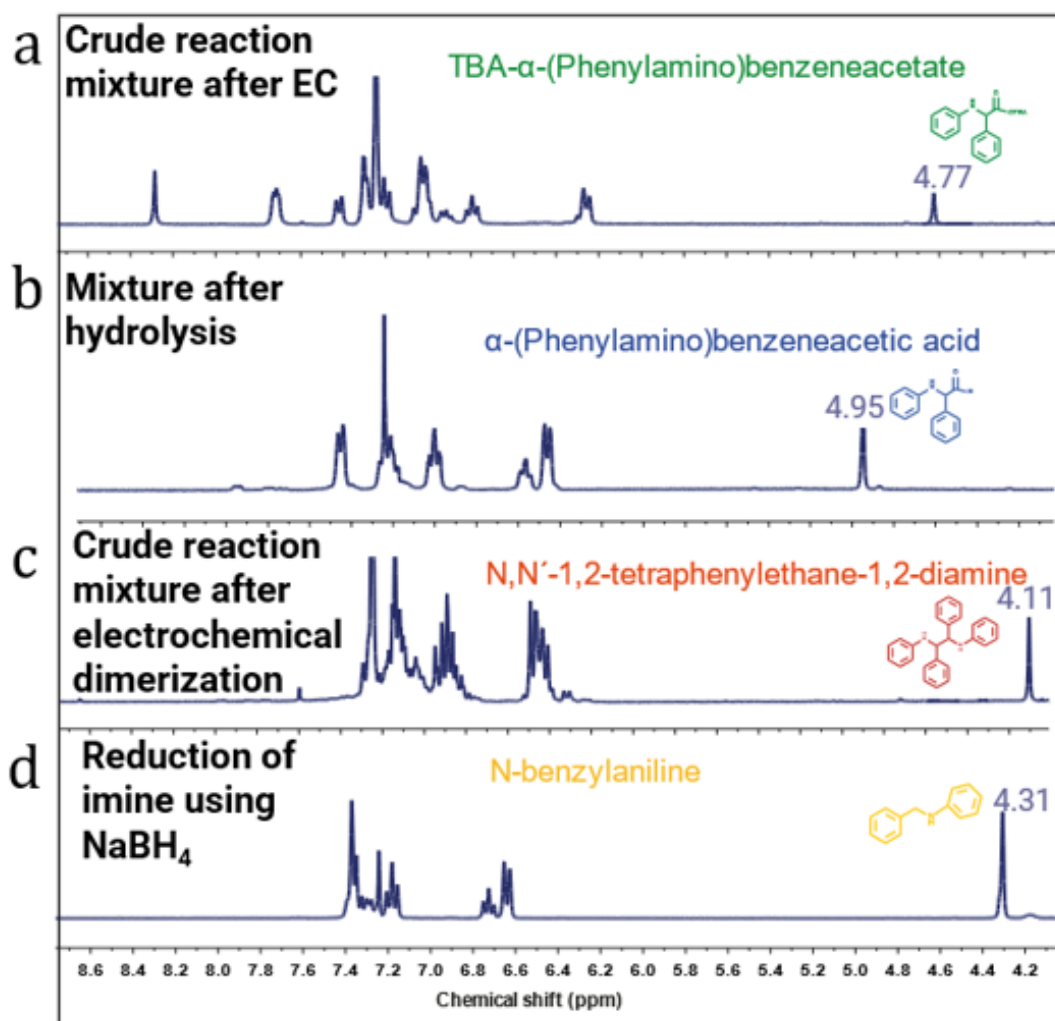
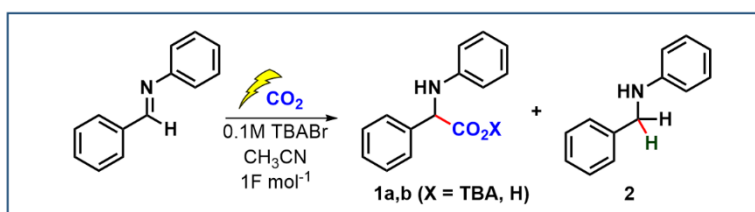


Figure 4. 14: Examples of NMR spectra of (a) crude reaction mixture after EC, (b) reaction mixture after the hydrolysis, (c) crude reaction mixture after electrochemical hydrodimerization of N -benzylideneaniline at -2 V in the absence of CO_2 (Ar was used instead), and (d) reaction mixture after the chemical reduction of N -benzylideneaniline by NaBH_4 .

were assigned to TBA salt of α -AA **1a** (PhCH(CO₂TBA)–NHPh, peak at 4.77 ppm) and product of hydrogenation product **2** (PhCH₂–NHPh, peak at 4.3 ppm). The third peak at 5.0 ppm was assigned to α -AA **1b** ((PhCH(CO₂H)–NHPh), which was confirmed by comparison of the crude reaction mixture and the purified by hydrolysis and extraction α -AA (Figure 4.14). Notably, the radical dimerization product **3** has not been detected (Figure 4.14). To determine the FE of EC and hydrogenation reactions, the NMR analysis of reaction mixtures with internal standard was carried out. The results are summarized in Table 4.1. The reaction selectivity showed high dependence on

Table 4. 1: The performance of different cathode materials in the electrochemical carboxylation of *N*-benzylideneaniline.



Entry	Cathode	Time (min)	E (V vs Ag/Ag ⁺)	FE _{1a+1b} (%) ¹	FE ₂ (%) ²	Selectivity (%) ³	FE _{CO} (%) ⁴	Total FE (%) ⁵
1	Ti	83	-1.52	95.5	3.0	96.9	1.5	100
2	Zn	77	-1.49	93.4	3.2	96.7	1.8	98.4
3	Ag	67	-1.50	82.9	13.8	85.7	3.3	100
4	Ni	108	-1.53	76.9	14.0	84.6	5.6	96.5
5	Fe	79	-1.44	73.5	14.1	83.9	1.5	89.1
6	Cu	94	-1.53	67.1	21.7	75.6	7.3	96.1
7	Au	95	-1.52	65.0	25.0	72.2	3.9	93.9
8	Pd	96	-1.50	60.0	25.1	70.6	3.0	88.1
9	Pt	110	-1.54	51.2	36.6	58.3	4.3	92.1
10	GC	112	-1.47	32.3	53.8	37.5	2.2	88.3
11	Sn	57	-1.53	11.7	83.6	12.3	3.4	98.7

The reactions were performed at imine reduction peak potential until passing charge of 1 F mol⁻¹.

¹The faradaic efficiency of electrocarboxylation products, which is equal to the EC yield calculated considering that only 50% of imine can be maximally converted after passing charge of 1 F mol⁻¹.

²The faradaic efficiency of hydrogenation. ³The imine reduction selectivity calculated as FE_{1a+1b}/(FE_{1a+1b}+FE₂). ⁴The faradaic efficiency of CO. ⁵The total FE calculated as sum of faradaic

efficiencies of electrocarboxylation, hydrogenation and CO₂ reduction. GC corresponds to glassy carbon in this table.

the catalyst nature. Zn and Ti showed the highest FE of EC (up to 95.5%) with over 96% selectivity, while glassy carbon and Sn showed the lowest FE of EC (11.7–32.3%) with selectivity below 40%. The FE of CO in all cases ranged from 1.5% (Ti) to 7.3% (Cu) and was negligible compared to the total FE of imine reduction. The values of FE of EC gradually decreased as follows: Ti (95.5%) > Zn (93.4%) > Ag (82.9%) > Fe (73.5%) > Cu (67.1%) > Au (65.0%) > Pd (60%) > Pt (51.2%) > GC (32.3%) > Sn (11.7%). The FE of hydrogenation increased gradually in the same order. Although the electrochemical behavior of imines was similar for all metals (Figure 2b), the results of potentiostatic electrolysis were dependent on the catalyst nature, indicating that the coordination of radical anion intermediate at the catalyst surface plays a crucial role in the reaction selectivity. Further studies supported by DFT calculations are required to better understand the role of the catalyst surface in the aforementioned electrochemical transformations, which is beyond the scope of this work.

As mentioned above, the mechanism of EC depends on the applied potential: at about -1.5 V EC proceeds mainly through the activation of imine, while at more negative potentials the

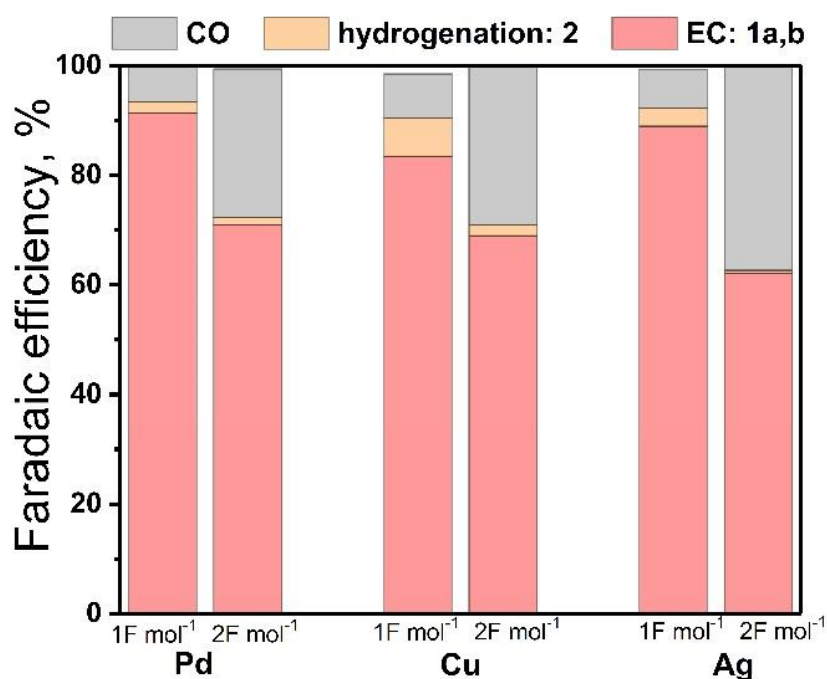


Figure 4. 15: The product distribution in electrochemical carboxylation of *N*-benzylideneaniline performed using different cathode materials at -2 V after passing charge of 1 F mol⁻¹ and 2 F mol⁻¹.

reaction occurs *via* activation of CO₂ followed by the coupling of CO₂^{•-} with imine. The dominance of the latter mechanism at high negative potentials is likely related to the favorable adsorption of carbon dioxide to the electrode surface in this potential range, which was previously discussed in detail on example of EC of organohalides.^{76,280} To elucidate the effect of the applied potential on the product distribution, we performed a series of potentiostatic electrolyses of *N*-benzylideneaniline in the presence of CO₂ at -2 V using Pd, Cu and Ag as cathodes (Figure 4.15). For all tested metals, the FE of competing hydrogenation process after passing 1 F mol⁻¹ decreased from 21-25% to 2-7% compared to the electrolysis at -1.5 V. The noticeable increase in the EC selectivity indicated the dominance of the mechanism *via* CO₂ activation, where hydrogenation reaction is not possible. Interestingly, the FE of CO was still low and ranged from 6 to 8%. Suppressed direct CO₂ reduction to CO during the EC can be related to the faster coupling of CO₂^{•-} with imine molecule compared to the coupling with CO₂ molecule that leads to the formation of CO. However, with the depletion of imine, the FE of CO increased dramatically and reached 27-38% after passing 2 F mol⁻¹. Overall, the increase in applied potential had a positive impact on the selectivity of imine reduction to corresponding carboxylic acid, but at the same time significant amount of charge was consumed for competing CO₂ reduction, decreasing the overall energy efficiency of the system. To overcome this issue, catalysts with high selectivity towards EC and high activity at low applied potentials must be developed.

4.4 Summary

In this chapter I demonstrated the main patterns in the electrochemical reduction of organic halides and imines in the presence and absence of CO₂ at different metal and carbon-based electrodes.

Specifically, for organohalides, I was able to map the specific electrochemical properties of different metal electrodes, such as potentials zones for the efficient one- and two-electron reductive cleavage of C-Hal bond, and the potential windows where the CO₂ electrochemical activation does not occur. I demonstrated that both the nature of the cathode material and the nature of an organic halide significantly affect the outcome of the reduction process. First, I showed that the reduction of R-Hal on non-catalytic metals (Fe, Al, Sn, Zn, and Ti) requires high energy input and leads to the formation of R⁻ species. Second, I found that Ag, Au, Cu, Pt, Pd, and in some cases Ni and Pb show noticeable catalytic activity towards the reduction of Ph-CH₂Br, Me-C₆H₄-CH₂Br and Ph-CH(Me)Br with ΔE_p values of up to 0.8 V compared to non-catalytic glassy carbon. In contrast to the aforementioned benzylic bromides, the reduction of NC-C₆H₄-CH₂Br requires less energy input, but still yields R⁻. However, in this case only Ag showed a moderate catalytic activity with ΔE_p of 0.18 V. Third, I showed that, in contrast to Ph-CH₂Br, the reduction of Ph-CH₂Cl proceeds at more negative potentials and yields R⁻ without an intermediate formation of R[•]. Finally, I demonstrated that at high negative potentials competing CO₂ reduction to CO₂^{•-} is observed, which lowers the FEs of EC. We showed that for typical catalysts of choice for EC (e.g. Ag) the potential gap between CO₂ electroreduction and EC is narrow with ΔE < 0.3 V, while for less common catalytic metals for EC such as Ni and Pb ΔE > 0.5 V.

For the EC of imines, I showed the wide applicability of the sacrificial anode-free approach that was proposed in Chapter 3. Additionally, I found that, similarly to organohalides, the nature of catalyst material significantly affects the selectivity of EC of imines: for some metals EC is a dominant process (Ti, Zn with up to 97% selectivity), while for other materials the hydrogenation of imine is a dominant process (glassy carbon with 88% selectivity). On the example of polycrystalline Pd, Cu, and Ag, I showed that the reaction mechanism changes with increasing potential, and at -2 V reaction proceeds with high contribution of CO₂ activation mechanism.

Chapter 5 Nanoscale catalysts for EC: surface chemistry, surface morphology, and stability

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Contribution: Performed conceptualization, investigation, visualization, formal analysis., and manuscript writing.

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Contribution: Performed material synthesis and characterization.

5.1 Introduction

In Chapter 4 I demonstrated that the nature of metal used as a cathode significantly affects both the current density and selectivity of the EC of organohalides and imines. By analogy with the catalyst improvement strategies for the electrocatalytic reactions in aqueous media, further advances in the catalyst design for EC can be achieved by the employment of the nanoscale electrocatalysis.²⁸¹⁻²⁸³ Notably, the electrochemical performance is not only affected by the increased surface roughness, but also by the exposed crystal facets that depend on NP shape.^{284,285} However, besides facets, a change in the NP morphology often leads to the difference in surface chemistry dependent on the selected production method. At present, the effect of the surface morphology difference as well as surface chemistry variability on the EC outcome is poorly understood. Disentangling the effects of surface atomic structure (i.e., voids, extrusions, facets, undercoordinated sites, etc.) and surface adsorbates (i.e., ligands originating from the NP synthesis) is essential for rational catalyst design, that would synergistically combine both the metal nanoscale and atomic surface structure and the molecular surface functionalization to achieve desired activity and selectivity in EC. Additionally, understanding the structural stability of electrocatalysts in a course of EC is of great importance as high activity of nanoscale materials can be accompanied by increased atomic mobility.^{286,287}

In this chapter I discuss the performance of nanoscale materials in the EC of benzylic bromides and imines. I focus on the effects of NP surface chemistry and morphology on the EC

outcome as well as study the stability of NP shape in the course of EC. To determine the effect of surface chemistry on the EC selectivity and activity I compared cetylpyridinium chloride (CPC) and citrate-capped Au NPs. To evaluate the effect of NP surface morphology on the EC outcome, I performed 3 series of nanomaterial comparisons: (1) Au branched NPs (Au BNPs) with long and short branches, Au spheres (Au NSs), Au nanocubes (Au NCs) and Au core-cages (Au CCs) for the EC of benzylic bromides; (2) Cu raspberry-like NPs (RLs), Cu cages (Cu CGs), and Cu NCs for the EC of (1-bromoethyl)benzene; (3) Pd BNPs and Pd NCs for the EC of N-benzylideneaniline. Finally, I evaluated the nanomaterial stability for all types of mentioned materials.

5.2 Au NPs for EC of benzylic bromides

5.2.1 Effect of surface chemistry on the Au NP performance in EC

5.2.1.1 Catalyst material synthesis and electrode preparation

To explore ligand-specific behavior of electrocatalysts for EC, we selected gold as a cathodic material due to its great performance in the EC of organohalides based on the bulk metal studies discussed in the Chapter 4 and reasonable stability.²⁸⁶ We produced near-spherical Au NPs (Figure 5.1) using two of the most common wet synthesis routes: Turkevich method resulting in a citrate-capped Au NPs (Au-citrate) and seed-mediated synthesis in aqueous solution of cationic surfactant – cetylpyridinium chloride (CPC) – leading to Au NPs stabilized with micellar double layers (Au-CPC). Both approaches were carefully adjusted to yield comparable NP sizes resulting in Au-citrate with the size of 53 ± 9 nm (Figure 5.1c) and Au-CPC with the diameter of 52 ± 1.5 nm

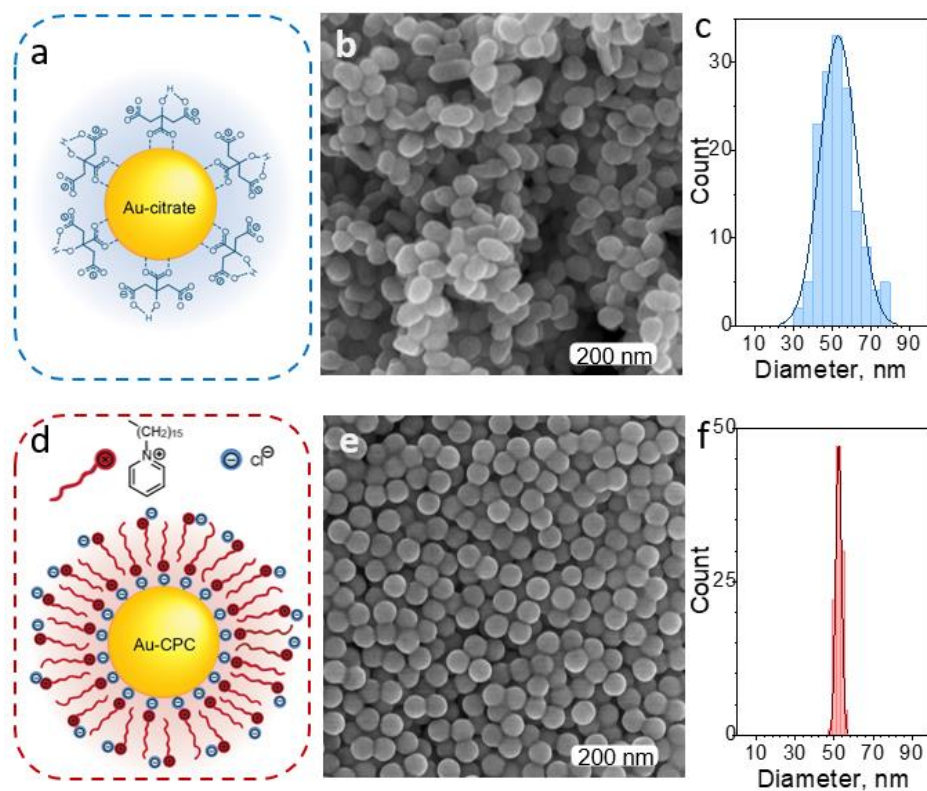


Figure 5. 1: Au nanoparticles chosen as objects for this study. (a,d) Schematics representing Au NP stabilization for Au-citrate (a) and Au-CPC (d). (b,e) SEM images of Au-citrate (b) and Au-CPC (e). (c,f) NP size distribution for Au-citrate determined *via* ≥ 150 measurements (c) and Au-CPC determined *via* ≥ 100 measurements (f).

(Figure 5.1f). Synthesized nanoparticles were concentrated and deposited on $0.5 \times 0.5 \text{ cm}^2$ Ti foil substrate using drop-casting with an even coverage and mass loading of about 1 mg cm^{-2} .

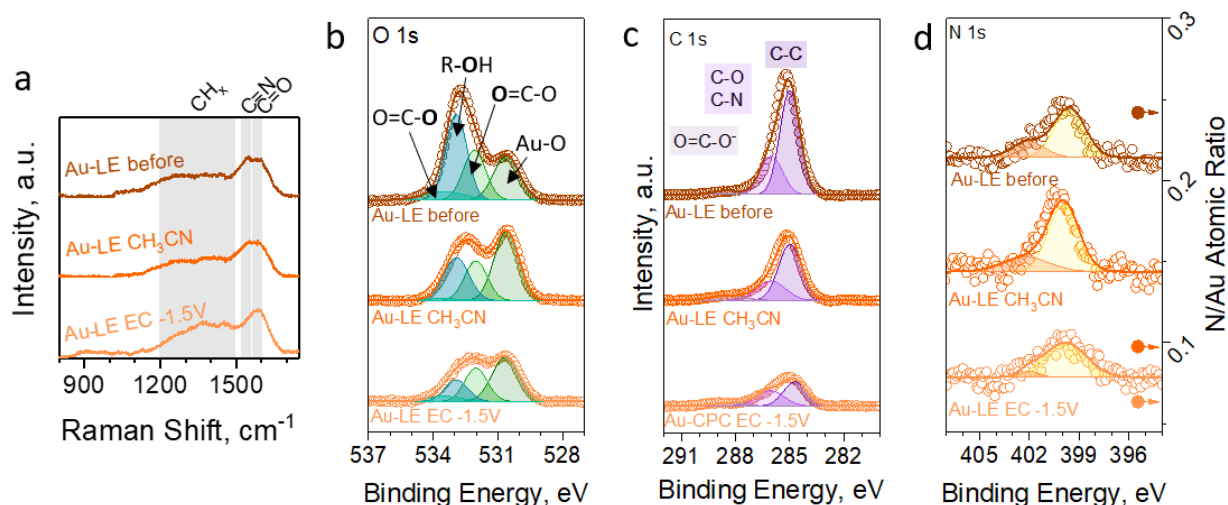


Figure 5. 2: Assessment of the Au-LE surface chemistry. Raman spectra (a) and XPS for O 1s (b), C 1s (c), and N 1s (d). Brown traces correspond to as prepared Au-LE, bright orange traces correspond to Au-LE extensively washed with acetonitrile, and light orange traces correspond to the Au-LE surface after EC for 1 h at -1.5 V vs Ag/Ag⁺.

In contrast to Au-CPC, Au-citrate is polycrystalline and includes grain boundaries²⁸⁹ that potentially can affect its electrocatalytic properties. To effectively isolate the surface chemistry effects, we synthesized a reference material introducing citrate molecules as adsorbates on Au-CPC. We employed direct ligand exchange on dried Ti-supported Au-CPC using 100 mM sodium citrate solution. The surface chemistry of resulting ligand exchanged Au NP electrode (Au-LE) represented a mixture of that of Au-CPC and Au-citrate, which was confirmed by Raman spectroscopy and XPS that showed both the presence of N (C=N bonds) from CPC and O from carboxylate (Figure 5.2).

To ensure that prepared electrodes have similar surface area of exposed gold for electrochemical reactions, we employed a common surface characterization method for Au-based electrodes: Pb underpotential deposition (Pb_{UPD}, Figure 5.3).²⁹⁰ Based on the Pb stripping curves, all three samples showed similar electrochemically active surface areas (ECSAs) and the surface was comprised mostly of mixed low index facets. Next, electrodes were studied in EC of benzyl bromide using CV and CA techniques.

5.2.1.2 Electrochemical performance

As nanoparticles inevitably would have higher activity compared to bulk materials of the same nature, we needed to carefully assess organohalide and CO₂ activation potential regions to have high selectivity of our target process – EC. To determine these potential zones corresponding to the path 1 and 2 (short drawing of the mechanism is depicted on the Figure 5.4a) of the EC we performed CV studies (Figure 5.4b). As EC *via* R-X activation requires lower applied potential than that via CO₂ activation, we determined the potential range where CO₂ activation does not occur by performing CV in CO₂ saturated solution of inert electrolyte (0.1 M TEABF₄) in CH₃CN.

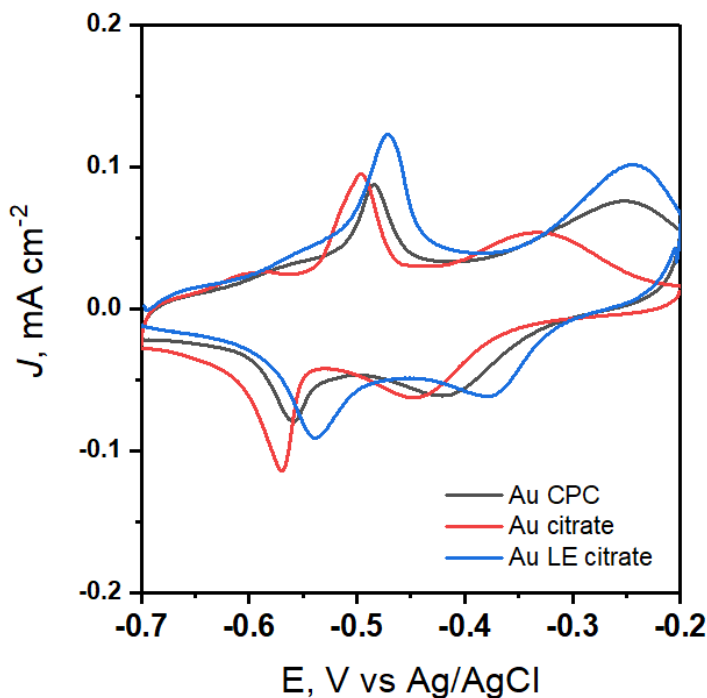


Figure 5. 3: Pb_{UPD} of Au nanoparticle electrodes with a loading of 1 mg cm⁻². Au-CPC (black trace), Au-citrate (red trace), and Au-LE (blue trace). CV was recorded in 0.1 M NaOH with the addition of 1 mM Pb(NO₃)₂ at a scan rate of 20 mV s⁻¹.

The onset potentials for CO₂ reduction for all studied Au NPs were about -1.38 V vs Ag/Ag⁺ and potentials at 5 mA cm⁻² were -1.51 V vs Ag/Ag⁺. Au-citrate NPs showed a 15 mV earlier onset of CO₂ activation. To determine the electrochemical behavior of benzyl bromide on Au-CPC and Au-citrate we carried out CV studies of the Ar-saturated solution of 0.1 M TEABF₄ in CH₃CN with the addition of 25 mM benzyl bromide. Notably, the peaks corresponding to the first and second electron transfers to benzyl bromide were overlapped, which means that the two steps described

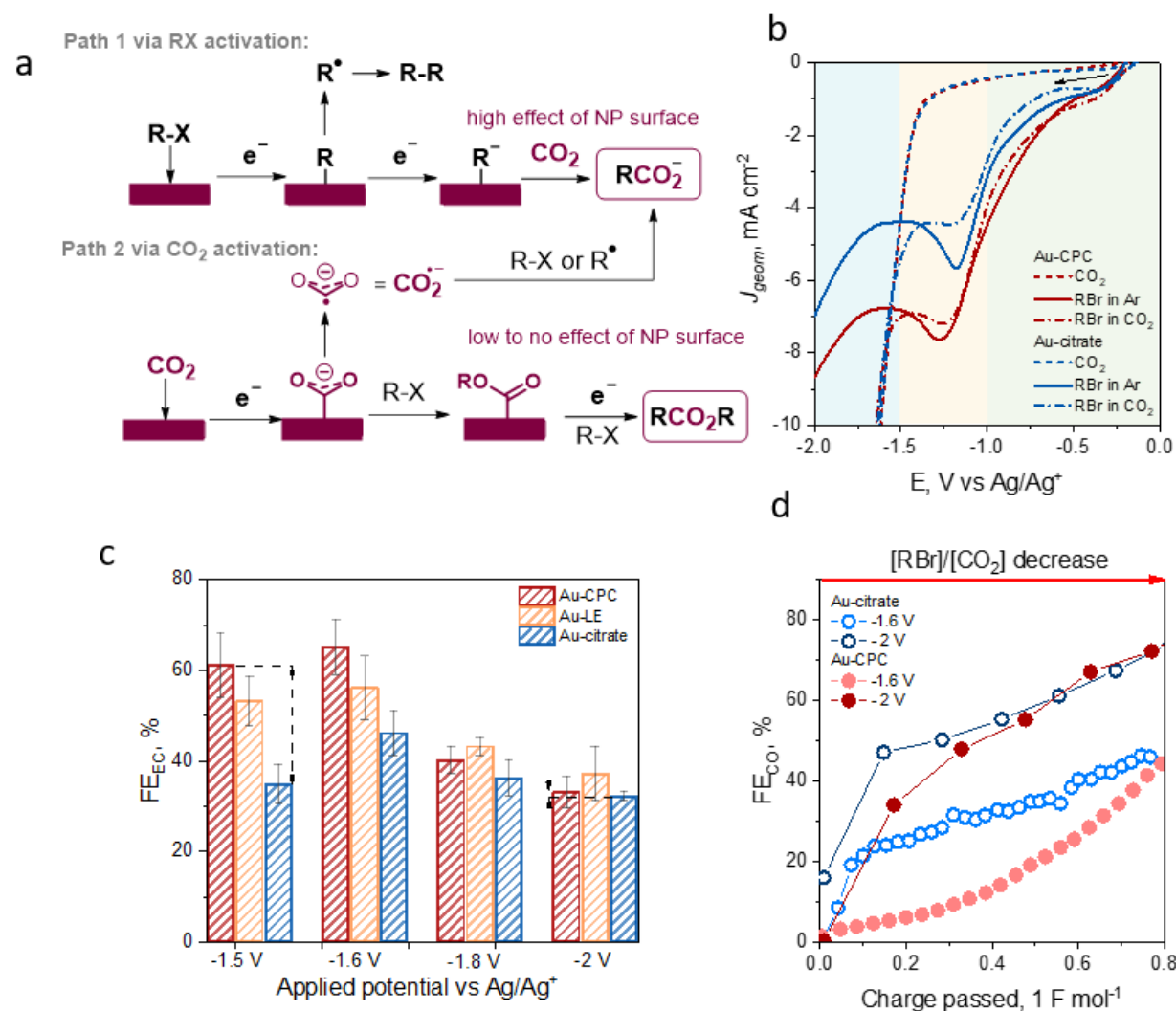


Figure 5. 4: Effect of Au nanoparticle surface chemistry on the EC outcome (a) Shortened mechanism of benzyl bromide electrocarboxylation (b) CV in 0.1 M TEABF₄ in CH₃CN at 50 mV s⁻¹. Potential zones are colored as follows: the adsorption of benzyl bromide and first electron transfer is green, second electron transfer is yellow, and CO₂ activation is blue. (c) FE of carboxylate after 1 F mol⁻¹ have been passed under constant applied potential in 25 mM benzyl bromide in TBABr in CH₃CN. (d) FE of CO during EC at different applied potentials.

above happen subsequently. We observed an earlier onset on Au-CPC for the benzyl bromide reduction by about 70 mV and a higher current density of the two-electron transfer peak by 35% compared to that of Au-citrate. In the case of CO₂ saturated solution of benzyl bromide, cathodic sweep for Au-CPC was similar to the one without CO₂ at potentials ≥ -1.6 V vs Ag/Ag⁺. At the same time, Au-citrate showed a drastic decrease in the benzyl bromide reduction activity in the

CO₂ saturated solution at all potentials suggesting enhanced CO₂ adsorption. We selected the potentials of interest for the potentiostatic electrolyses based on the determined boundaries (Figure 5.4 b) and target current densities above 5 mA. To represent dominant R-X and CO₂ activation pathways the respective potentials of -1.5 and -2 V vs Ag/Ag⁺ were selected. Additionally, to assess the change of the reaction selectivity for the potential window where both pathways are enabled, the potentials of -1.6 and -1.8 V vs Ag/Ag⁺ were selected.

To evaluate the selectivity of EC on Au nanostructured electrodes with different surface chemistry, potentiostatic electrolyses were performed on freshly prepared electrodes to eliminate the possibility of the surface chemistry fluctuations. All reactions were carried out under the constant delivery of CO₂ at a rate of 14 sccm in the solution of 0.1 M TBABr in CH₃CN with the starting benzyl bromide concentration of 25 mM. Figure 5.4c shows resulting FEs of carboxylate after 1 F mol⁻¹ equivalent of electrons was passed. Interestingly, when CA was performed at -1.5 V vs Ag/Ag⁺, a drastic difference in the EC selectivity was noticed between Au-CPC, Au-LE, and Au-citrate cathodes with respective carboxylate FEs of 61%, 53%, and 34%. The results show that the NP surface chemistry significantly affected the preferential adsorption and the energy barriers required for R-X activation with citrate being less favorable than CPC for this process. For the more negative applied potential of -1.6 V vs Ag/Ag⁺ we expected a similar dependence of the reaction outcome on the Au NP surface chemistry considering low CO₂ activity at this potential

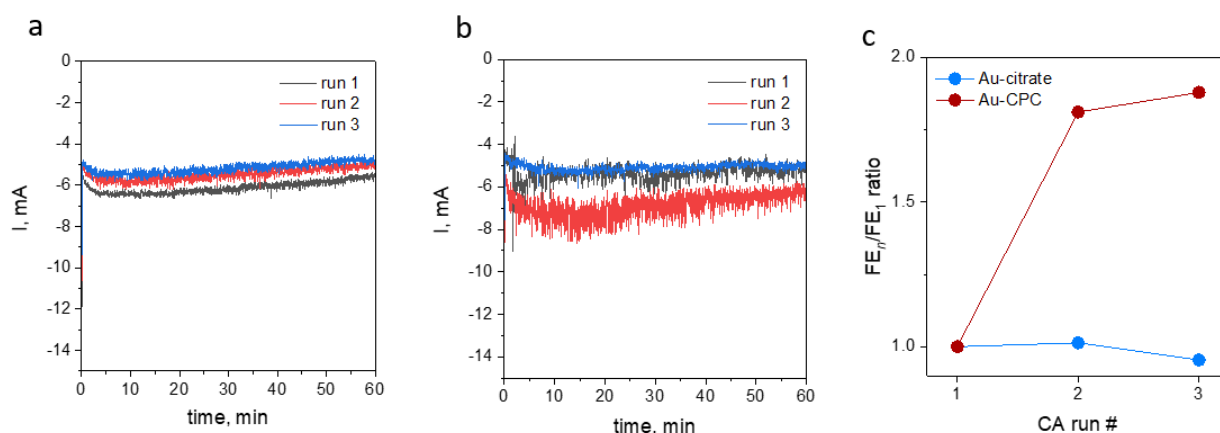


Figure 5. 5: Electrode stability in EC during short term electrolysis. (a,b) Consecutive 1 h CAs under typical EC conditions at -1.5 V vs Ag/Ag⁺ for Au-CPC electrode (a) and Au-citrate electrode (b). (c) Carboxylate FE change upon the electrode repeated use.

and EC FEs trend for R-X activation pathway. Indeed, electrolyses at -1.6 V vs Ag/Ag⁺ showed

the highest EC FE for Au-CPC followed by Au-LE and Au-citrate. Overall, a slight decrease in the applied potential resulted in slightly higher FEs of carboxylate (by 5-12%) for all tested Au NP cathodes. We believe that it happens due to the facilitated second electron transfer at higher energies decreasing the contribution of the $R^{\bullet}$ -driven side reactions. At more negative applied potentials of -1.8 and -2 V vs Ag/Ag^+ , where the impact of the CO_2 activation pathway was expected to be more prominent, only a small difference in the EC FEs was observed between all studied Au NP cathodes. For CAs at -1.8 and -2 V vs Ag/Ag^+ the respective EC FEs for Au-CPC were 40% and 33%, which were comparable to 36% and 32% for Au-citrate. The obtained FE data suggests that Au NP surface chemistry has little to no effect on the CO_2 activation pathway of EC.

As the selectivity of EC, especially at low applied potentials, depends on the electrocatalyst selectivity towards R-X or CO_2 adsorption we aimed to compare the behavior of Au-CPC and Au-citrate towards the side reaction of CO_2 electroreduction at low and high applied potentials. Preferential CO_2 adsorption and activation can be assessed based on the rate of direct CO_2 reduction to CO during EC. We monitored the FE of CO as a function of the passed charge during the EC of benzyl bromide using in-line GC. The experiments were conducted at -2 V vs Ag/Ag^+ representing high CO_2 reactivity region as well as at -1.6 V vs Ag/Ag^+ where CO_2 reduction rate is minimal. At -2 V no significant difference was observed after passing 10 C (the first 20 minutes of the reaction). At -1.6 V FE of CO for Au-citrate was high from the beginning of the electrolysis and increased from 20% to 46% in the course of electrolysis, while FE of CO on Au-CPC was negligible in the beginning and increased exponentially with the benzyl bromide depletion. The observed trends indicate that at all studied potentials Au-citrate has an enhanced affinity to CO_2 , which can be attributed to their higher hydrophilicity compared to the Au-CPC surface and partial negative surface charge.

To evaluate surface chemistry stability in the course of EC, we first performed three 1-hour consecutive electrolyses under EC conditions at -1.5 V vs Ag/Ag^+ (Figure 5.5). Even though CA curves were somewhat similar for all runs for both Au-CPC and Au-citrate, in the case of Au-CPC FE of carboxylate increased by a factor of 1.8 for the second and 1.87 for the third electrolysis run compared to the FE of the first short term CA. This change in the EC outcome signifies a rapid change in the Au-CPC cathode surface chemistry associated with the applied current. Interestingly, Au-citrate showed stable FE of carboxylate regardless the number of runs.

5.2.1.3 Catalyst surface characterization

To further understand the evolution of the NP surface chemistry in the aprotic media and under the EC conditions, we studied Au-CPC and Au-citrate electrodes using ex-situ Raman spectroscopy and XPS and determined general changes after the materials were exposed to acetonitrile and to the EC conditions at -1.5 V vs Ag/Ag⁺ for 1 h (Figure 5.6).

First, spectroscopic studies were performed for Au-citrate electrode. The surface of freshly prepared electrode was evaluated by Raman spectroscopy (Figure 5.6a) showing a band at around 1600 cm⁻¹ which was attributed to C=O stretching of citrate carboxylic groups.²⁹¹ The detailed examination of the surface with XPS revealed peaks characteristic to that of adsorbed citrate molecules. Specifically, XPS spectrum of O 1s (Figure 5.6d) showed four peaks at 530.6 eV, 532 eV, 532.9 eV, and 533.5 eV that respectively correspond to Au-bound oxygen (O_{Au}), C=O of carboxylic group, oxygen of alcohol group, and C-O of carboxylic group.²⁹² XPS spectrum of C 1s (Figure 5.6e) revealed three peaks at 284.5 eV, 286 eV, and 288.5 eV that were assigned to C-C/C-H, C-O of alcohol group, and the carbon of carboxylic group, respectively.²⁹³ Notably, XPS signal for Au 4f (Figure 5.6c) showed that Au-citrate was comprised of Au⁰ with some oxidized Au surface that behaves as adsorption sites for citrate.²⁹⁴

After the Au-citrate electrode was extensively washed with acetonitrile, we have not observed any qualitative changes in both Raman spectrum and XPS spectra. However, the quantitative analysis of XPS data showed approximately 30% decrease in C/Au and O/Au (Figure 5.6i) ratios hinting at the loss of some citrate molecules from the surface. Interestingly, the O_{Au}/Au ratio remained the same suggesting that only not surface-bound citrate molecules were removed from the surface by the washing with acetonitrile.

Next, we examined the Au-citrate electrode that was exposed to EC conditions at -1.5 V vs Ag/Ag⁺ for 1 h. We noticed a decrease in C=O signal in Raman spectrum. Additionally, XPS data indicated dramatic changes in the organic species present on the surface. Namely, inspecting both XPS spectra of O 1s and C 1s, we noticed the decrease in the O_{Au} and CO₂⁻ signals and the increase in the peaks related to alcohol group (R-OH, C-O). This hints at the partial electroreduction of carboxylic groups to alcohols in the adsorbed citrate molecules. Another noticeable change was the 2-fold increase in carbon content, specifically, in C-C/C-H peak. As no nitrogen was detected by XPS, this carbon cannot originate from the electrolyte (TBA⁺) or solvent, thus, we hypothesize that this increase in C content is related to the presence of the products and intermediates of

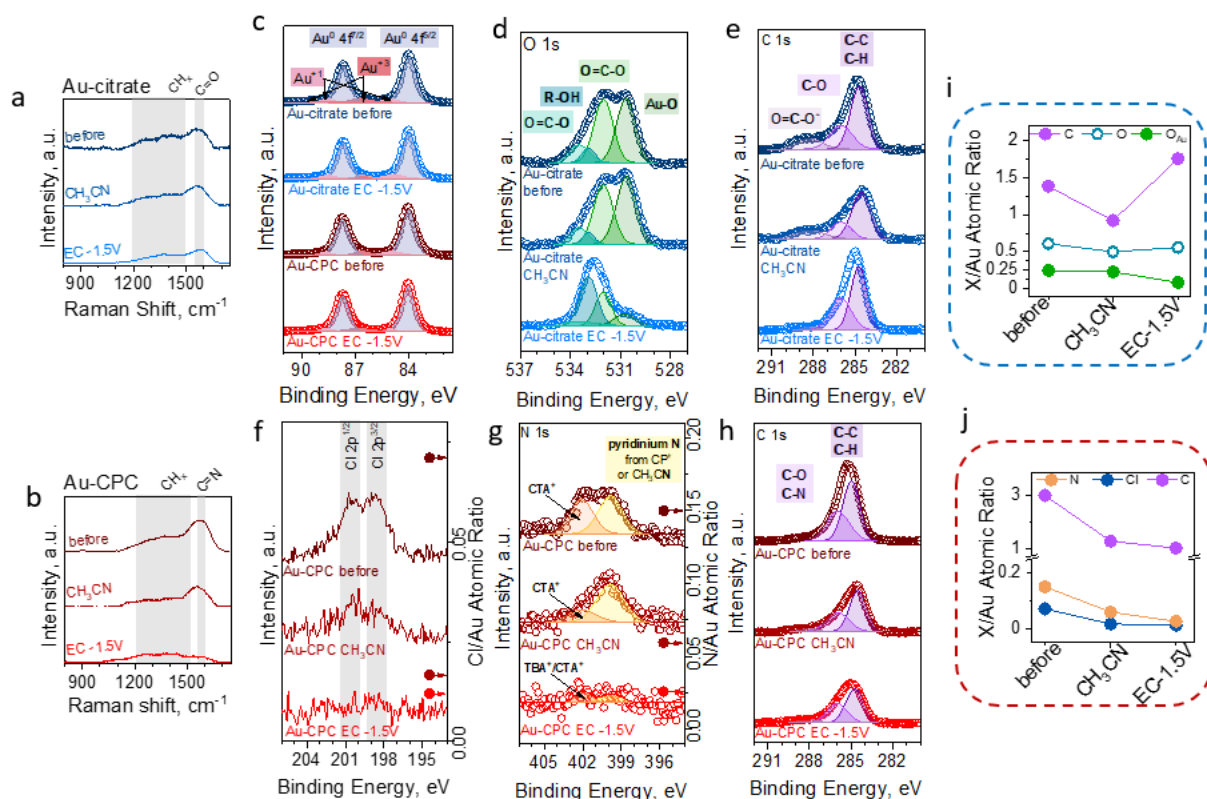


Figure 5. 6: Spectroscopic assessment of the electrode surface chemistry. **(a-b)** Raman spectra of **(a)** Au-citrate and **(b)** Au-CPC electrodes as prepared (before), after extensive washing with acetonitrile (CH_3CN), and after EC CA at -1.5 V vs Ag/Ag^+ for 1 h followed by thorough washing with CH_3CN . **(c-h)** XPS evaluation of the electrode surface for Au-citrate and Au-CPC: Au 4f peaks **(c)**; O 1s fitted data for Au-citrate electrode **(d)**; C 1s fitted data for Au-citrate **(e)** and Au-CPC **(h)**; Cl 2p data for Au-CPC electrodes **(f)** with the corresponding Cl/Au atomic ratios calculated from XPS; N 1s data for Au-CPC electrodes with the corresponding N/Au atomic ratios calculated from XPS **(g)**. For all fitted XPS datasets raw data are depicted as hollow circles, fitted peaks are colored, and fitted data are shown as a bold trace. **(i)** C/Au (violet trace), O/Au (blue trace with hollow circles), and $\text{O}_{\text{Au}}/\text{Au}$ (green trace) ratios calculated from XPS for Au-citrate electrode. **(j)** C/Au (violet trace), Cl/Au (deep blue trace), N/Au (orange trace), and $\text{O}_{\text{Au}}/\text{Au}$ (green trace) ratios calculated from XPS for Au-CPC electrode.

electroorganic reaction on the Au-citrate surface even after the extensive washing with acetonitrile. Overall, citrate is strongly bound to Au surface and only undergoes chemical reductive modifications of carboxyl groups under applied potential, notably, without any significant effect on the material electrocatalytic properties.

Second, we studied the behavior of Au-CPC electrode. The as-prepared electrode showed characteristic band at 1560 cm^{-1} in Raman attributed to C=N stretching of pyridinium group (Figure 5.6b).²⁹¹ Further evaluation of the surface chemistry composition was performed by XPS showing the presence of Cl (Figure 5.6f) and Br (Figure 5.7). Additionally, XPS spectrum of N 1s (Figure 5.6g) showed the signals of quaternary ammonium (402 eV) and pyridinium (399.8 eV) nitrogens that respectively correspond to CTAB and CPC – cationic surfactants used during the synthesis of Au-CPC.²⁹⁵

After the Au-CPC electrode was washed with acetonitrile we have not noticed the disappearance of C=N stretching band on Raman. The analysis of XPS data showed noticeable

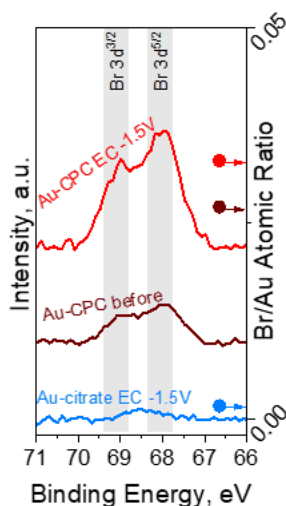


Figure 5. 7: XPS evaluation of adsorbed Br based on the Br 3d peak for Au-CPC and Au-citrate electrodes.

decrease in Cl 2p, N 1s, and C 1s (Figure 5.6h) peaks along with the approximately 3-fold decrease in Cl/Au, N/Au, and C/Au ratios (Figure 5.6j) that indicates that micellar double layer was destroyed and any unbound to Au surfactant molecules were removed.

Lastly, we evaluated the surface chemistry of Au-CPC electrode that was exposed to EC conditions at -1.5 V vs Ag/Ag^+ for 1 h. Raman spectroscopy showed the disappearance of C=N signal. Further investigation by XPS also confirmed the decrease in N and Cl content on the Au surface to trace amounts, however, Br 3d peaks were still present (Figure 5.7) and Br/Au ratio increased by 20% due to the remaining surface-bound Br from the initial surface functionalization and additional adsorption of Br from the electrolyte and benzyl bromide during the EC. Interestingly, while N/Au ratio decreased more than 2 times, C/Au ratio decreased only by 20%

hinting that cationic surfactants are not the main source of C on the surface after EC. In analogy with Au-citrate, we believe that remaining carbon is related to the products and intermediates of the electrochemical reaction. Notably, the presence of small amount of quaternary ammonium N in N 1s XPS suggests that some electrolyte may be adsorbed to the surface. Overall, in the case of Au-CPC, the double layer of micelles is destroyed once the material is introduced into a polar organic solvent leaving only a monolayer of adsorbed surfactant molecules on the Au surface. Further this adsorbed surfactant is being stripped from the Au surface during EC leaving only Br and reaction-related molecules on the surface. The removal of surfactant layer plays a crucial role in the great electrocatalytic behavior of Au-CPC in EC.

5.2.2. Effect of Au NP morphology on the Au NP performance in EC

Next, we aimed to determine the effect of Au NP surface morphology on their performance in the EC of organohalides. To this end, we synthesized the series of Au NPs of various shapes (Figure 5.8) in aqueous solutions of cationic surfactants that was determined above to be the most attractive medium for the fabrication of cathodic materials for EC. We followed the same electrode

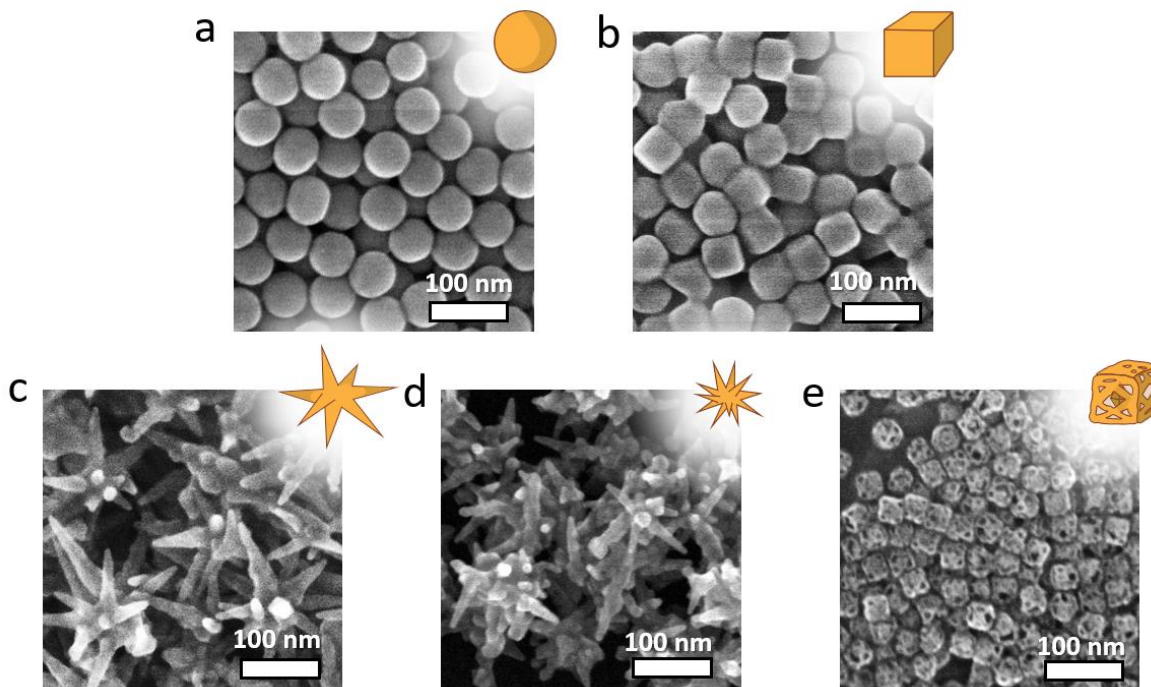


Figure 5. 8: Au NPs of various morphologies synthesized in aqueous solutions of cationic surfactants. SEM images and corresponding cartoons for Au NSs (a), Au NSs (b), Au BNPs with long (c) and short (d) extrusions, and Au CCs (e).

preparation protocol and used the same cell design as in the subchapter 5.2.1. To remove most of

the surfactant molecules from the NP surface, an additional wash with methanol was performed before the use of the electrodes.

To determine potentials for the activation of organobromides we performed CV in Ar-saturated inert electrolyte 0.1 M TEABF₄ in ACN with 25 mM additives of the corresponding organobromides (Figure 5.9). We used Au foil and Au-citrate electrodes for reference. Figure 5.9d,f,h and 5.9e,g shows summarized first and second electron transfer peak potentials,

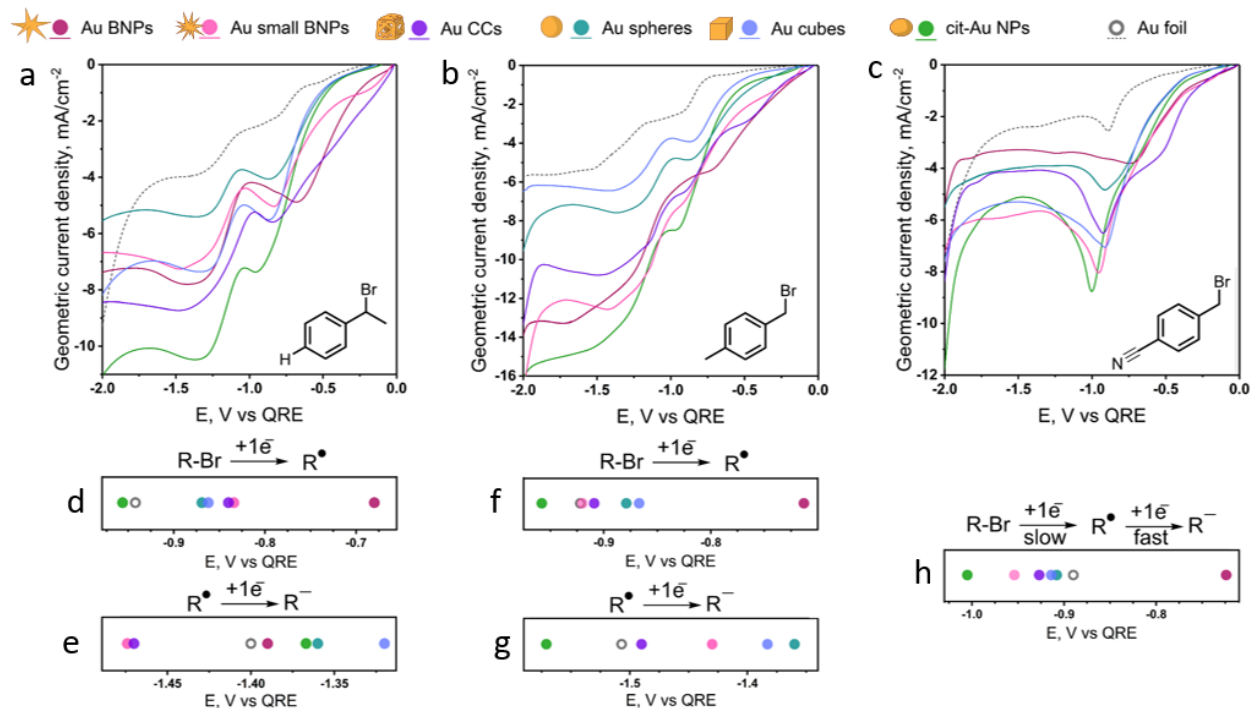


Figure 5. 9: The effect of Au NP morphology on the organobromide reduction. (a-c) LSVs for organobromide reduction in Ar-saturated 0.1 M TEABF₄ with 25 mM organobromide additive at a scan rate of 20 mV s⁻¹. (d-h) the position of the first and second electron transfer peaks for the organohalide reduction determined from the LSVs a-c.

respectively. Interestingly, 4-(bromomethyl)benzonitrile (Figure 5.9c,h) showed only one sharp peak as it has a strong EWG, thus, once first electron transfer happens, second electron transfer proceeds almost subsequently.⁸⁹ Among all studied NPs, Au BNPs showed the lowest peak potential for the first electron transfer, which is predictable due to the presence of extrusions and associated field enhancement effect.¹¹³ However, no trend was found for the second electron transfer peak and peak positions had narrower distribution than that for the first electron transfer for both (1-bromoethyl)benzene and 1-(bromomethyl)-4-methylbenzene. That difference in the

electrocatalytic behaviour of the studied catalysts towards the two mechanistic steps suggests that the electrochemical hotspots play a crucial role for the first electron transfer and have no particular

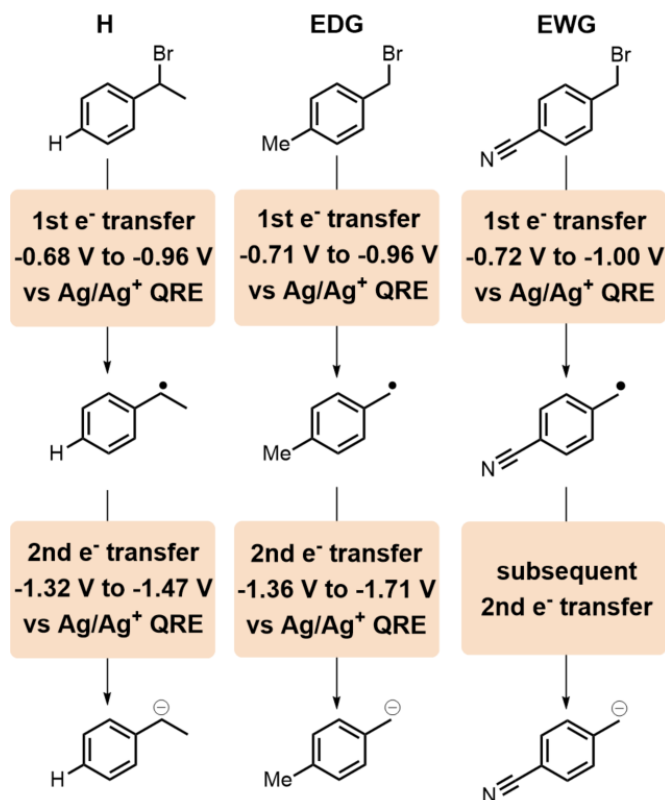


Figure 5. 10: The summary of potential intervals for the activation of studied organobromides on different Au nanomaterials.

influence on the further reduction of the formed radical intermediate. First and second electron transfer ranges on Au NPs are summarized on the figure 5.10.

To assess EC selectivity, we performed a series of potentiostatic electrolyses. As Au BNPs showed the highest activity towards the initial organobromide activation, we chose them as materials for the potentiostatic studies. We performed CAs using CO_2 -saturated 0.1 M TBABr solution in ACN as electrolyte under the constant delivery of CO_2 into the catholyte at a rate of 14 sccm with the additive of 25 mM of the corresponding organohalide. The effect of applied potential on the distribution of organohalide reduction main products is depicted on the Figure 5.11.

We chose very low applied potentials to target organohalide activation as the field enhancement on the sharp tips works for all species present in the reaction mixture and the onset

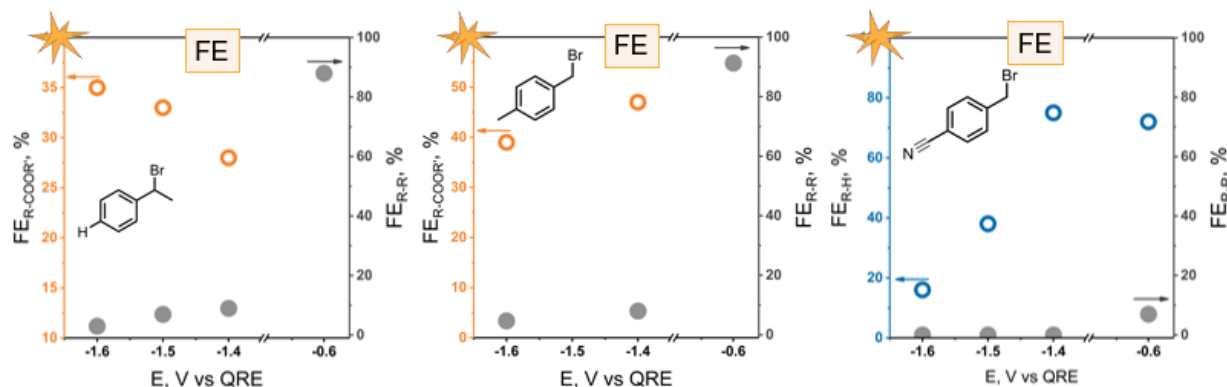


Figure 5. 11: The distribution of organobromide reduction products with corresponding FEs after potentiostatic electrolyses at various potentials using Au BNPs with long branches as cathode materials.

potential of CO₂ activation on Au BNPs was observed about 100-200 mV before all other studied Au-based nano and bulk materials.

Both (1-bromoethyl)benzene and 1-(bromomethyl)-4-methylbenzene showed quite low FE of EC product (below 40%) at all studied potentials due to the high competition with the direct CO₂ electroreduction that, as we hypothesise, was enhanced on the sharp tips even at low applied potentials. Thus, Au NPs especially with extrusions have high selectivity towards CO₂ electroreduction and are not the most promising electrocatalysts for the EC.

No carboxylate formation was observed for the EC of 4-(bromomethyl)benzonitrile at all studied potentials. Moreover, at -0.6 V vs Ag/Ag⁺ only about 8% of the dimerization product was observed. Instead for all studied potentials we observed the formation of the product of protonation R-H suggesting that reaction follow a slightly different mechanism for molecules substituted with EWG in para position. In addition, the CN group itself can participate in electrochemical reduction complicating the reduction process.

5.2.3 Stability of Au NPs in the course of EC: the effect of adsorbed reaction intermediates

To further evaluate the feasibility of the NP use in EC we studied their surface morphology evolution and overall structural stability in the course of the reaction. First, we evaluated changes in the surface morphology of the Au NPs after the series of CV experiments using Pb_{UPD} (Figure 5.12). Overall, after 20 CV cycles, which were depicted on the Figure 5.9, only Au CCs had significant change in their Pb_{UPD} traces signifying the change in the type of electrochemically

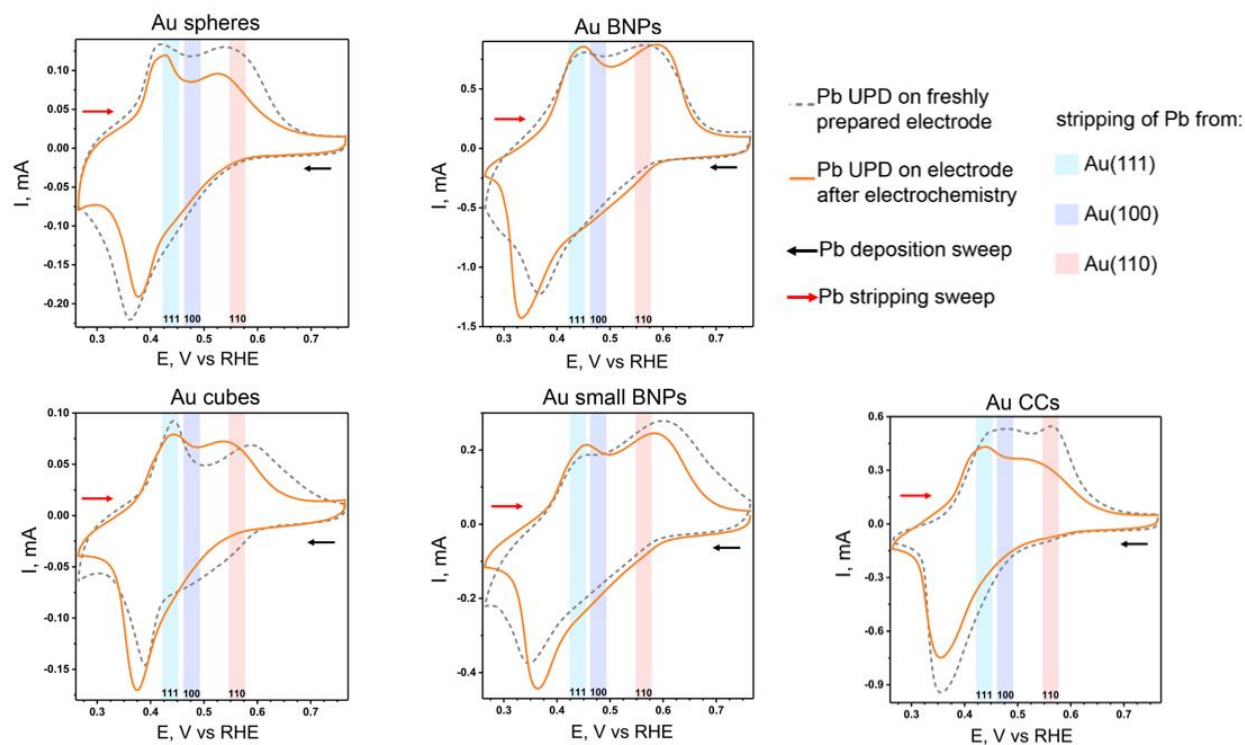


Figure 5. 12: Pb underpotential deposition performed on Au electrodes with various surface morphology before and after cyclic voltammetry studies. Potential regions attributed to Pb stripping from low index facets are colored (blue for Au(111), violet for Au(100), and orange for Au(110)).

available surface due to its reconstruction. Both Au BNPs showed no signs of the change in the exposed facets.

To get a further insight in a long term Au NP structure stability, we performed SEM imaging of the electrodes before and after EC. We performed EC of 25 mM benzyl bromide in 0.1 M TBABr at -1.8 V vs Ag/Ag^+ for arbitrary Au NP shapes: Au NSs, Au BNPs, and Au CCs (Figure 5.13). In the case of Au NSs and Au BNPs after 240 C of charge was passed within 4 h and 3 h of the cell operation, respectively, only slight surface smoothing was observed, and overall NP integrity remained intact. In contrast, after 3 h of EC under the same conditions, Au CCs underwent significant shape degradation. The stability of both Au BNPs and Au CCs during EC followed the same trends that were observed for aqueous CO_2 electroreduction.²⁸⁶

In the case of aqueous CO_2 electroreduction, we demonstrated that surface-bound reaction intermediates have a strong effect on the atomic mobility and, thus, on the surface (in)stability. To

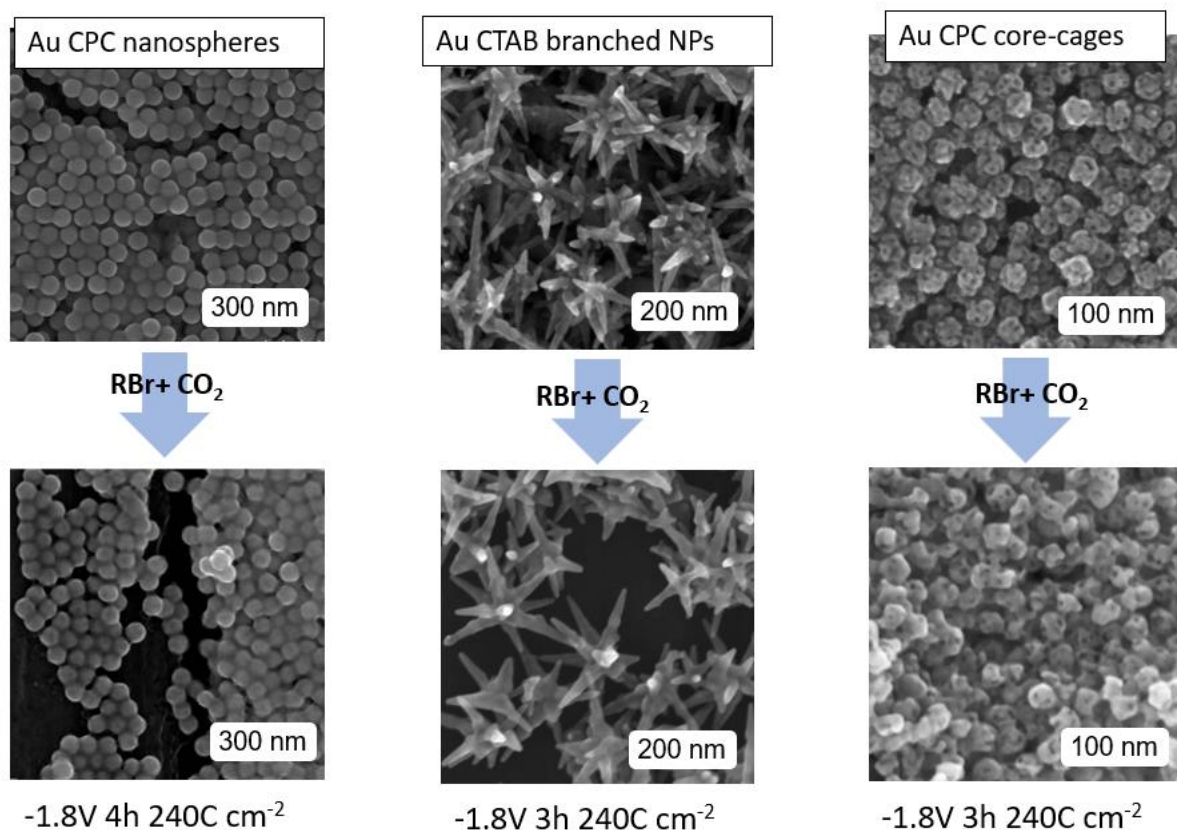


Figure 5. 13: The assessment of Au NP stability via SEM after full reaction of the EC of 25 mM solution of benzyl bromide in 0.1 M TBABr on the example of Au NSs, Au BNPs, and Au CCs. Passed charge, applied potential, and reaction time are stated for every reaction.

this end, we aimed to examine the effect of adsorbed surface species on the electrocatalyst stability during EC. As we previously discussed, the main intermediates in the EC of organohalides are either organic radicals and carbanions for the mechanistic path 1 or CO₂ radical anion for the path 2 (Figure 5.4). To isolate surface bound intermediates related to only one mechanistic pathway at a time, we carefully selected the reaction conditions where only one type of the species was present. We performed CAs using a potential where both pathways were enabled: -1.8 V vs Ag/Ag⁺. Also, we passed twice the charge of the experiments on the Figure 5.13 to have a more pronounced degradation. To evaluate the effect of organic radicals and carbanions on the Au CC stability we performed the reaction in the Ar-saturated solution of 50 mM benzyl bromide (Figure 5.14). To elucidate the effect of the CO₂^{•-} on the Au CC stability we performed the reaction in the CO₂-saturated solution of electrolyte in the absence of organohalide. Finally, we performed SEM imaging of these electrodes and noticed that Au CCs underwent severe surface reconstruction in

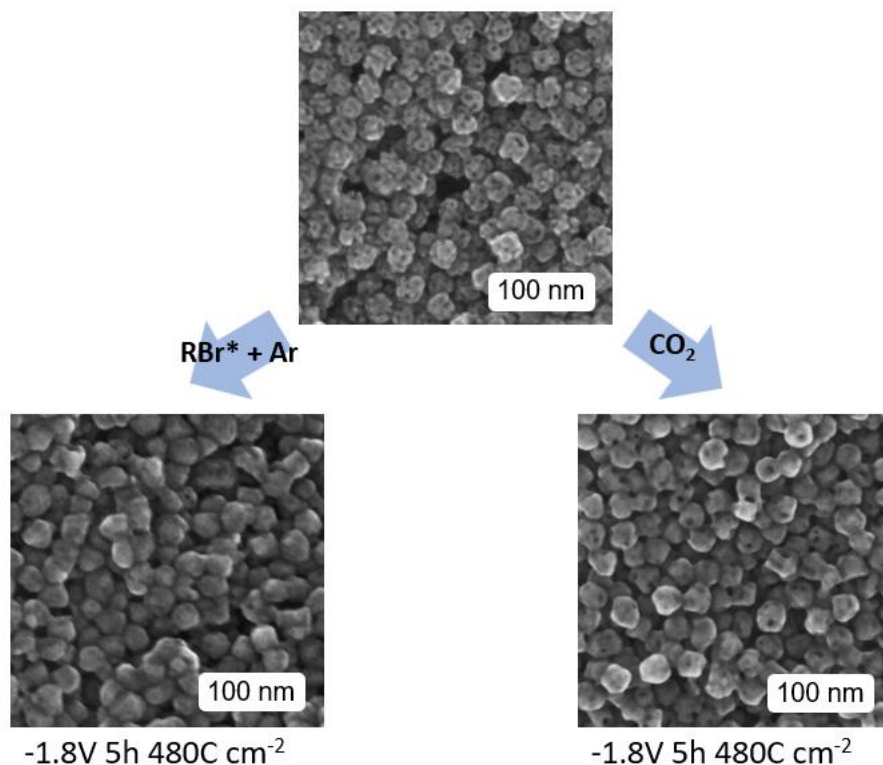


Figure 5. 14: The effect of adsorbed reaction intermediates on the Au CC stability. SEM images of Au CCs before electrochemistry and after homocoupling reaction in 50 mM solution of benzyl bromide in Ar-saturated 0.1 M TBABr in ACN or direct CO₂ electroreduction in CO₂-saturated solution of 0.1 M TBABr. In ACN. Passed charge, applied potential, and reaction time are stated for every reaction.

both cases. Interestingly, in the case of the simulated CO₂ activation mechanistic pathway some shape integrity such as holes remained, while in the case of organohalide activation pathway Au CCs completely lost their shape and resembled rough spherical particles. As was discussed for the Au NP degradation in aqueous CO₂ electroreduction,²⁸⁶ the driving force behind the atomic mobility facilitation by the adsorbed reaction intermediates is the intermediates' inductive effect that decreases the energy of the bonds in the metal lattice. And indeed, the observed degradation trend aligns with the charge stabilization capabilities of the mentioned reaction intermediates: PhCH₂^{•-} and CO₂^{•-}, with CO₂^{•-} being able to better stabilize the negative charge due to charge delocalization on two oxygen atoms *via* resonance. To summarize, NP stability in the course of EC depends on the NP shape and adsorbed reaction intermediates with the CO₂ activation pathway being preferable for the prolonged stability of the nanoelectrocatalyst.

5.3 Cu NPs for EC of benzylic bromides

In Chapter 4 we showed that bulk Cu cathodes showed high catalytic activity in the EC of organohalides. Thus, we aimed to further increase the EC selectivity and activity introducing Cu materials with nanoscale morphology as electrocatalysts. Considering the discussion in the subchapter 5.2.1, wet-chemical synthesis in aqueous solutions of cationic surfactants was of high interest as a strategy for obtaining Cu NPs.

5.3.1 Synthesis of Cu NPs in aqueous solutions of cationic surfactants

Generally, shape-controlled Cu NP synthesis relies on polydentate polymers²⁹⁶ or non-polar ligands^{297,298} which are difficult to remove post synthesis.²⁹⁹ This inevitable surface contamination is detrimental for catalytic applications, which require the catalyst surface structure to be fully accessible and compositionally well-defined.^{299,300} In contrast, NP synthesis using cationic surfactants in aqueous media, which relies on the colloidal stabilization of the NPs by the surfactant micelles, enables a facile removal of this surface functionality by a wash with alcohols that destroy the micelles.³⁰¹ This convenient surface purification strategy makes metal NPs synthesized using aqueous cationic surfactants an attractive material for electrocatalysis, however, only a limited number of Cu shapes has been reported using this general approach.²⁸⁸ Thus, to study the effect of Cu NP features on the outcome of EC we needed to first develop a tunable aqueous synthesis of Cu NPs with various shapes using cationic surfactants.

Reported aqueous synthesis methods for producing Cu NPs with surface stabilized by a double layer of cationic surfactants can be characterized by poor size and shape distribution.²⁸⁸ For instance, the synthesis of cubic NPs³⁰² lacks control over the balance between nucleation and growth, which leads to a poor shape selectivity and the formation of Cu nanowires as a side-product in large quantities (Figure 5.15). One way to overcome this challenge is by using a seed-mediated approach, as has been demonstrated to be successful for obtaining cubic Cu NP with surface stabilization by hexadecylamine.^{298,303} For seed-mediated Cu NP growth, Pd nanocubes are excellent seeds, as they can be easily obtained with cationic surfactant stabilization, their synthesis is simple, scalable and highly reproducible¹³¹ and Cu can be epitaxially grown on Pd due to having the same face-centered cubic lattice structure.²⁹⁸ In addition, Pd and Cu have a sufficient contrast in TEM that is convenient for locating the seed and examining Cu growth process.

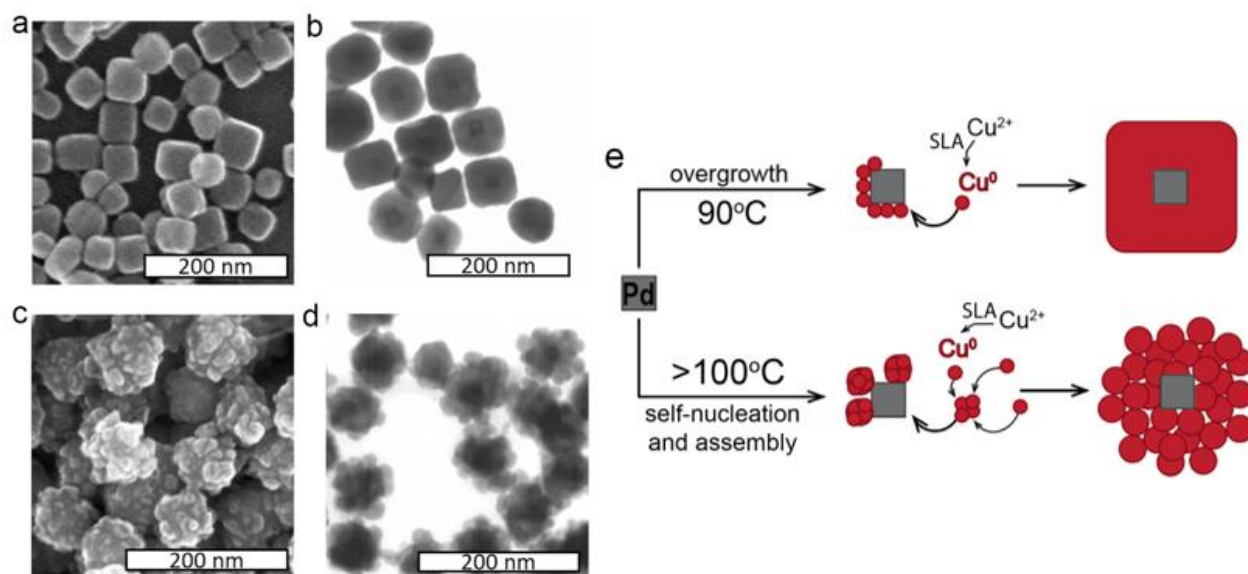


Figure 5. 16: Effect of the temperature on the Cu NP growth mechanism. SEM and TEM images of Cu NPs synthesized at 90 °C (a,b) and at 110 °C (c,d) oil bath temperatures. (e) Schematic of the proposed growth mechanism at different temperatures with indication of the reaction mixture temperature. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

When we performed seed-mediated reaction at the same conditions as the reaction without seeds, we found that the temperature regime in the seed-mediated synthesis of Cu NPs dramatically affected the growth mechanism, enabling high tunability of shape by adjusting the reaction temperature (Figure 5.16).

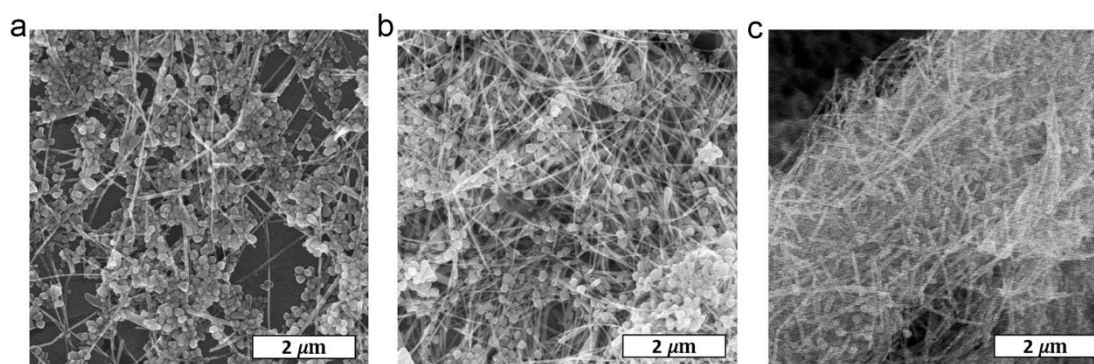


Figure 5. 15: SEM images of Cu NPs formed without Pd seeds in aqueous solution on CTAC. NP growth was conducted at 90 °C (a), 100 °C (b), 110 °C (c) in preheated oil bath in sealed scintillation vials for 1.5 h each. At temperatures below 90 °C the nucleation of Cu is negligible.

To understand the effect of the reaction temperature on the Cu growth mechanism, we performed the synthesis using different temperature regimes (Figure 5.16 and 5.17). First, we studied the particle formation at 90 °C: in the seedless approach, the reaction was proceeding for 1.5 h indicating that Cu self-nucleation is relatively slow and growth is favored at this temperature

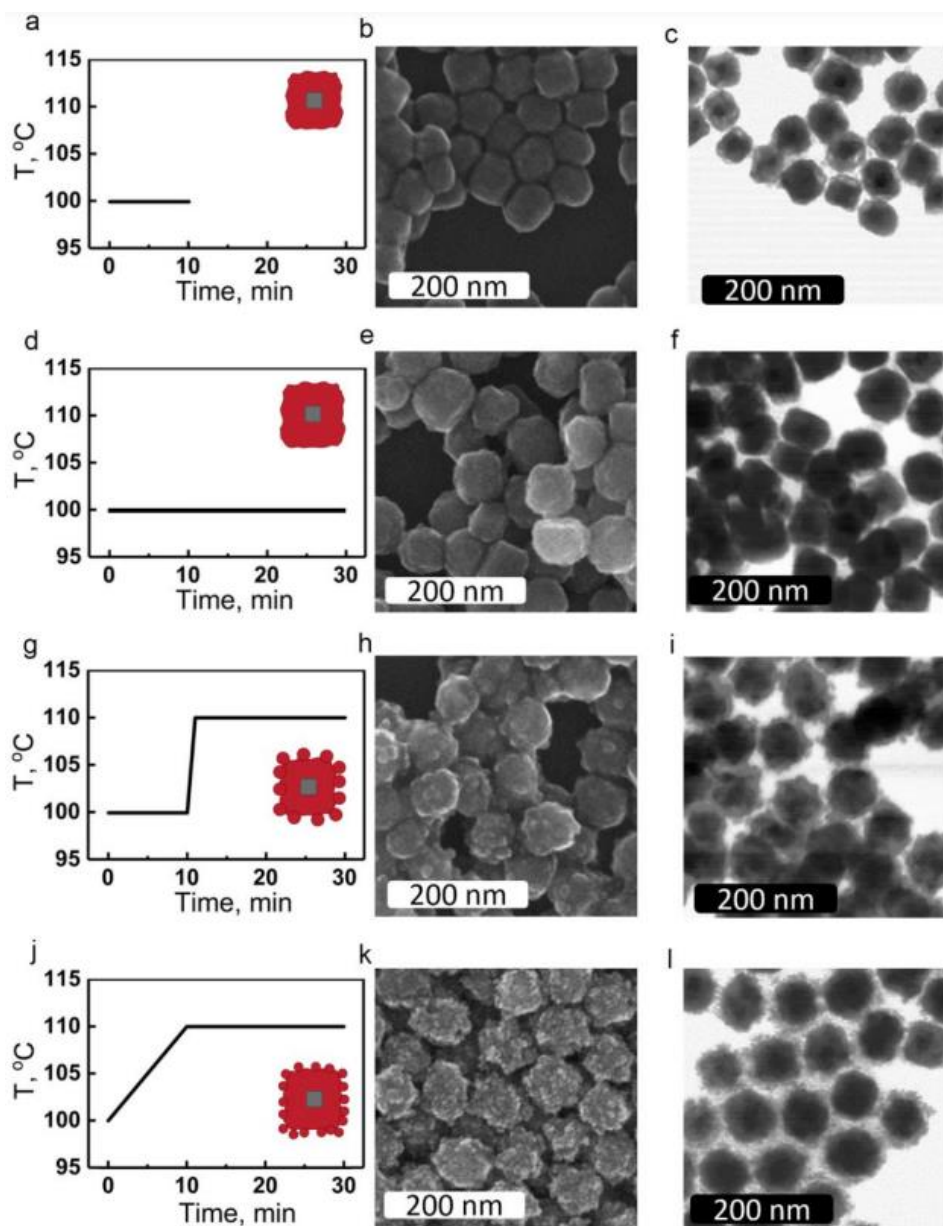


Figure 5. 17: The effect of the oil bath temperature on the Cu NP formation. Temperature regimes and formed particle cartoons (a,d,g,j), SEM images (b,e,h,k) and TEM images (c,f,i,l) of formed nanostructures. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

(Figure 5.15). In the seed-mediated approach, heteroepitaxial Cu growth on Pd seeds occurred without Cu self-nucleation, resulting in cubic Cu NPs with a Pd core inside each particle (Figure 5.16b). In the synthesis at 100 °C, the cubic definition of the formed NPs significantly reduced and spherical Pd-seeded Cu NPs were observed instead (Figure 5.17d,e,f), suggesting a shift from kinetically-controlled facet stabilization to thermodynamically controlled uniform growth.³⁰⁴ When the temperature of the oil bath was increased to 110 °C, we obtained raspberry-like Cu NPs comprised of small sphere-like Cu NPs (14 ± 3 nm, Figure 5.16a) around a cubic Pd core.

The XRD analysis of raspberry-like Cu NPs showed peaks of crystalline metallic Cu (Figure 5.18). We hypothesized that this NP shape was formed due to self-nucleation of Cu enabled at this elevated temperature, followed by assembly of self-nucleated Cu particles around Pd seeds

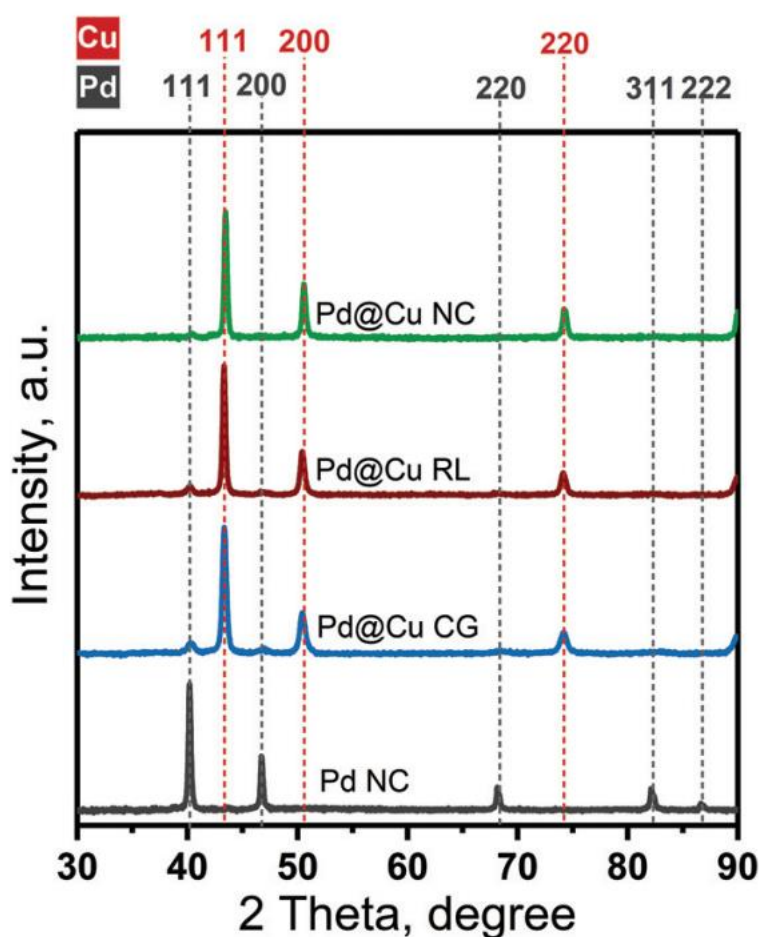


Figure 5. 18: XRD spectra of cubic Pd seeds (black trace) and as-synthesized and dried under argon atmosphere Pd@Cu NPs with different shapes. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

present in the solution. Indeed, small self-nucleated Cu NPs were observed in the reaction medium upon further investigation of the SEM images (Figure 5.19). The assembly of these small self-nucleated Cu NPs into larger clusters around Pd seeds could be associated with a high total surface area of the formed NPs and a low surfactant concentration in the reaction medium (Figure 5.16e).³⁰⁵⁻³⁰⁷ To further validate that this change in the growth mechanism is temperature-guided, we performed the synthesis for 10 minutes at 100 °C followed by 20 minutes at 110 °C (Figure 5.17g-i). In these experiments, the formation of a dense Cu shell around Pd seeds with a raspberry-like outer layer was observed, demonstrating that mixed morphologies between the cubic and spherical Cu NPs and the raspberry-like structures can be readily obtained using this synthetic methodology.

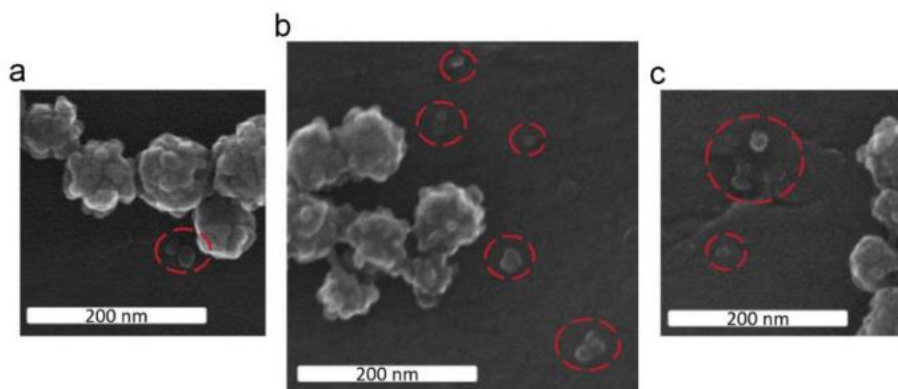


Figure 5. 19: SEM images of not assembled small Cu NPs formed during raspberry-like Cu NPs formation. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

As we hypothesized that the formation of raspberry-like NPs is associated with the lack of colloidal stabilization, we investigated the effect of the surfactant concentration and nature on the produced NPs keeping other reaction conditions the same. We found that already with a slight increase in the [CTAC]:[Cu] ratio only spherical NPs were formed (Figure 5.20b). Changing the surfactant from CTAC to CPC also led to the formation of spherical Cu NPs (Figure 5.20c,d). Additionally, we altered the Cu precursor to evaluate the effect of the counterion in the standard procedure for raspberry-like NPs. The replacement of Cu(OAc)₂ with Cu(NO₃)₂ showed no effect on the reaction outcome (Figure 5.21). When CuCl₂ was used, the synthesis yielded spherical NPs (Figure 5.20c) rather than raspberry-like NPs. This change can be attributed to the increased

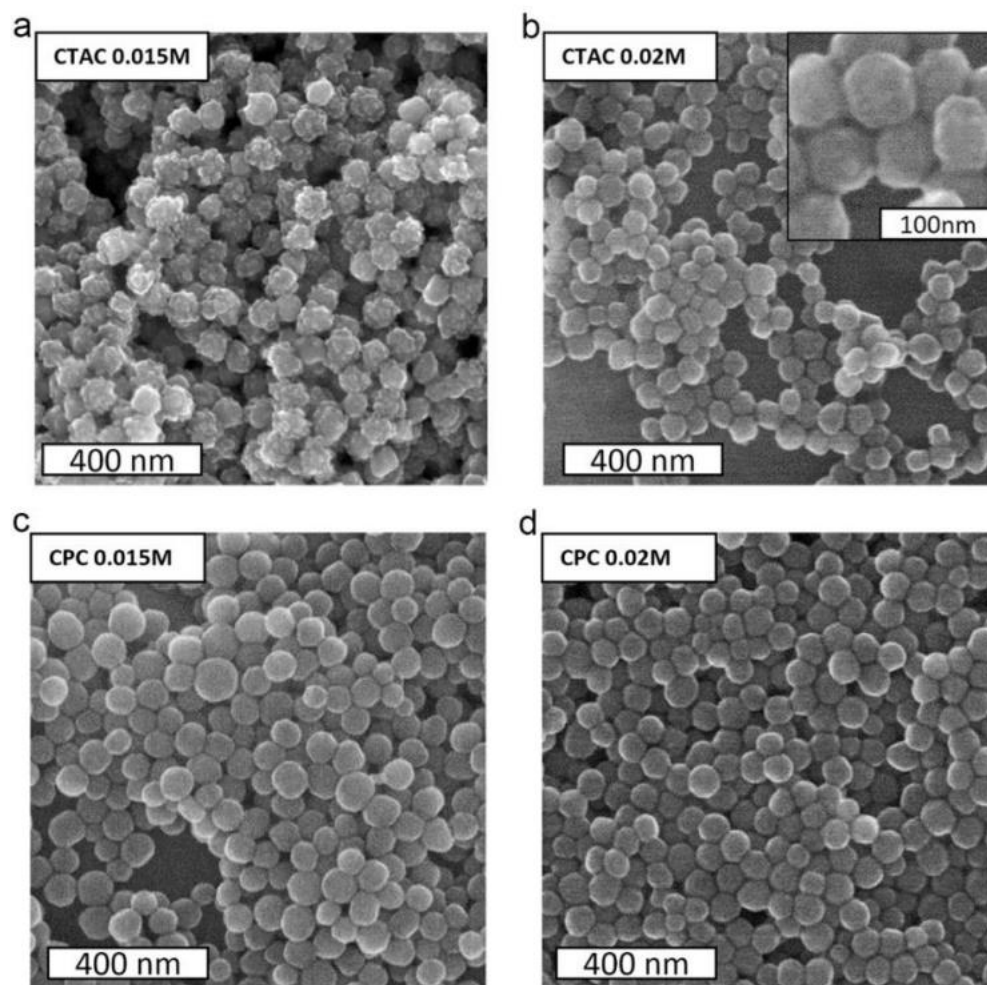


Figure 5. 20: The effect of surfactant nature and concentration on the standard raspberry-like NP synthesis. Cu NPs formed under standard reaction conditions (a), under higher CTAC concentration (0.02 M) with other conditions kept same (b), under standard reaction conditions with CTAC changed to equimolar CPC (c), under higher CPC concentration (0.02 M) with other conditions kept same (d). Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

concentration of Cl^- ions compared to the standard procedure with $\text{Cu}(\text{OAc})_2$ where Cl^- originated only from CTAC ($\Delta \sim 10\%$).

Next, we examined how the stirring of the reaction mixture affected the NP formation using the standard 110°C procedure for raspberry-like NPs. The reaction mixture turned from light-brown to yellow during the first 30 minutes of vigorous stirring, associated with the formation of Cu^{1+} ; when the stirring was turned off, the color rapidly changed to dark red indicating the

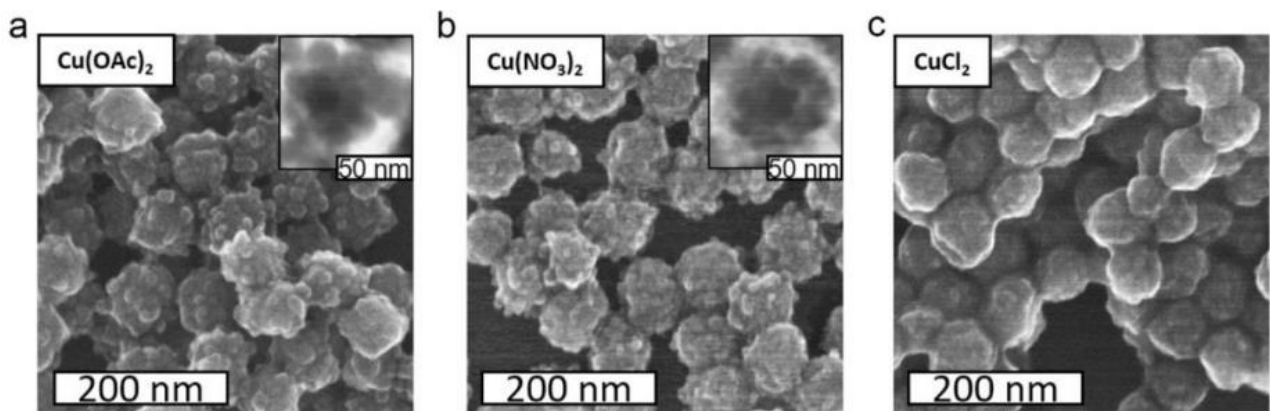


Figure 5. 21: The effect of Cu precursor anion on the Cu NP shape in standard synthesis of raspberry-like NPs. SEM images of Cu NPs synthesised using $\text{Cu}(\text{OAc})_2$ (a), $\text{Cu}(\text{NO}_3)_2$ (b), and CuCl_2 (c). Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry

formation of metallic Cu NPs that had the raspberry-like architecture. This difference in the reaction behavior can be attributed to the remaining oxygen in the headspace of the reaction vessel that was continuously enriching the reaction mixture under stirring and oxidizing Cu^0 , thereby preventing the formation of the target NPs.³⁰⁸ Importantly, NP etching occurred to some degree in all reactions with air in the headspace, with < 5% of hollow NPs observed during TEM analysis of the samples (Figure 5.22). These observations suggested that the presence of small quantities of oxygen in the solution resulted in the formation of a hollow interior rather than in the complete dissolution of the Cu NPs. To induce a more pronounced interior etching of NPs during the reaction while keeping the reduction rate high, we increased the headspace from 1 cm^3 to 7.5 cm^3 while immersing only a half of the reaction vessel into the oil bath. Under these conditions, Cu cages with continuous exterior walls and remnant internal Cu network (Figure 5.23) as well as partially

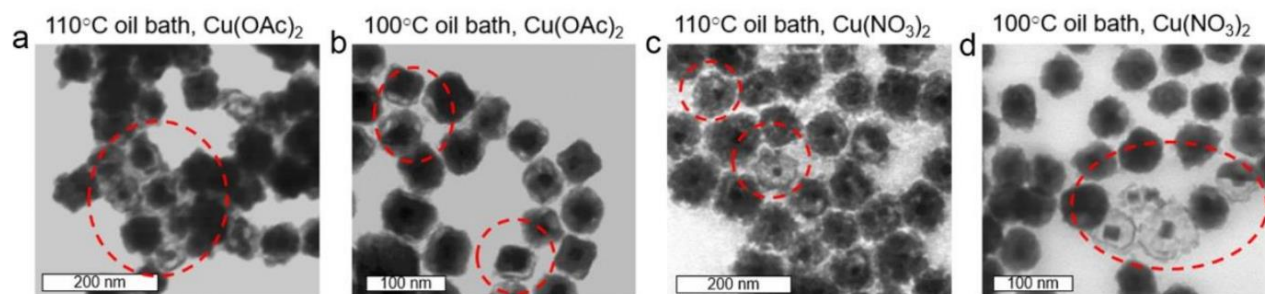


Figure 5. 22: TEM images of etched Cu particles found in different experiments (reaction conditions are shown above each image). Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

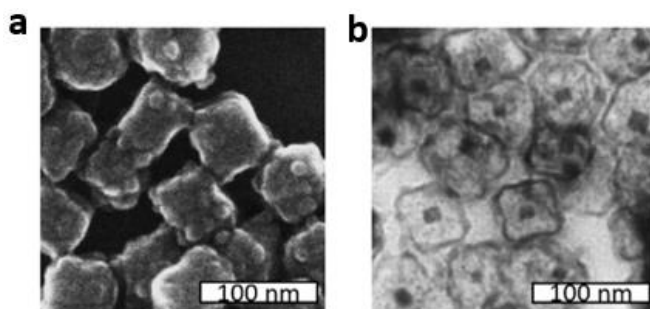


Figure 5. 23: The examples of Cu cages: SEM (a) and TEM (b) images. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

etched particles (Figure 5.24a-c) were obtained. These Cu cages (Figure 5.23) had a rough surface, centered Pd core and wall thickness of 3.8 ± 0.8 nm. We evaluated the shape purity of this synthesis by visual TEM image analysis, which revealed that significantly etched cages and partially etched NPs accounted for $\sim 33\%$ and $\sim 26\%$ respectively, while the rest of the NPs remained unetched based on the even density observed in the TEM images. Attempts to increase the shape purity by extending the reaction duration led to the collapse of the hollow particle likely due to a facilitated diffusion of Cu atoms (Figure 5.25). While Cu cages were not stable in solution for an extended period time, in a dry state when deposited on a substrate they remained structurally intact for at

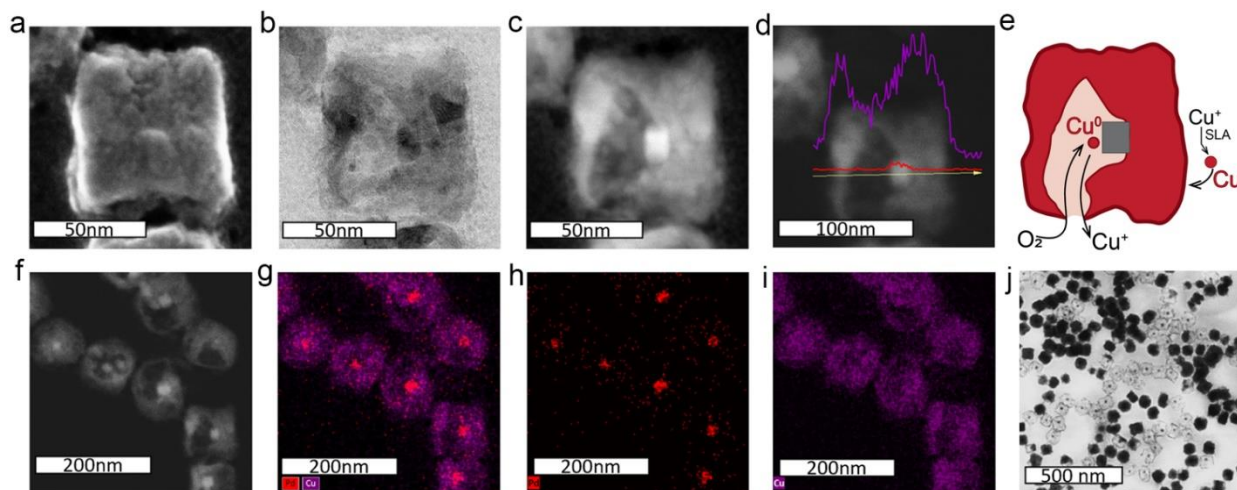


Figure 5. 24: In-situ etching of Pd seeded Cu NPs. SEM (a), TEM(b), dark field TEM (c), and EDX line scan (d) images of partially etched Cu NP. (e) Schematic of etching mechanism. Elemental composition of Pd (red) and Cu (purple): EDX mapping (f-i). (j) Low magnification TEM image for etching efficiency assessment. Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

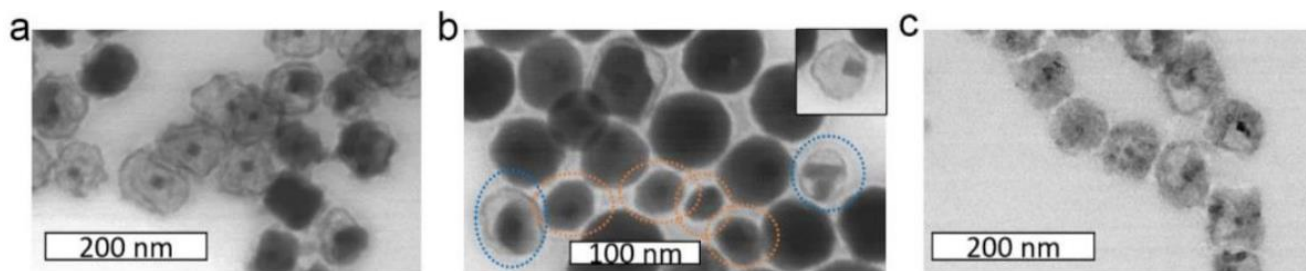


Figure 5. 25: The structural stability of Cu cages. TEM images of freshly prepared Cu cages (a), Cu cages left in ice-cold solution for 8 hours (b, orange dotted circles show collapsed cages, blue dotted circles highlight almost collapsed cages), Cu cages that were left for >1 year on a TEM grid on air (c). Reprinted with permission from ref. [288]. Copyright 2021, Royal Society of Chemistry.

least a year. Based on the detailed TEM image analysis of the synthesized Cu cages and previously reported data on using O_2 as an etchant for various metal NPs,^{309,310,311} we propose that oxygen dissolves the inner part of the particle while keeping the walls intact due to the presence of the reducing agent (SLA) near the outer surface of the particle (Figure 5.24e). The analysis of the chemical composition of the hollow Cu NPs by energy-dispersive X-ray spectroscopy (EDX) revealed that the NP consisted of Pd core, Cu-deficient inner area and a dense Cu shell (Figure 5.24g-i). A single-particle EDX line scan revealed a significant decrease in the Cu count in the inner area between the Pd core and the Cu shell (Figure 5.24d).

5.3.2 Cu NP performance in EC

After we synthesized a wide variety of Cu NPs stabilized by cationic surfactants, we decided to perform the EC of organobromides on the most intricate ones: RL NPs and CGs. We chose EC of (1-bromoethyl)benzene as our model reaction.

To assess the electrocatalytic activity of studied materials and choose an appropriate applied potential for EC, we performed CVs in CO_2 -saturated electrolyte to examine CO_2 electroreduction onset potential and corresponding current densities, Ar-saturated electrolyte containing RBr to determine first- and second-electron transfer onset and peak potentials, and CO_2 -saturated electrolyte containing RBr to find $J(E)$ relationships under EC reaction conditions (Figure 5.26b, Figure 5.27). The onset potentials of RBr reduction and CO_2 electroreduction were observed at ~ -0.7 V vs Ag/Ag^+ and ~ -1.2 V vs Ag/Ag^+ , respectively. Figure 5.26c shows the comparison of RBr reduction peaks and the electrocatalytic activities of Cu raspberry-like NPs, cages, and Cu foil towards $R^\bullet$ and R^- formation. On Cu foil, two distinct reduction peaks were

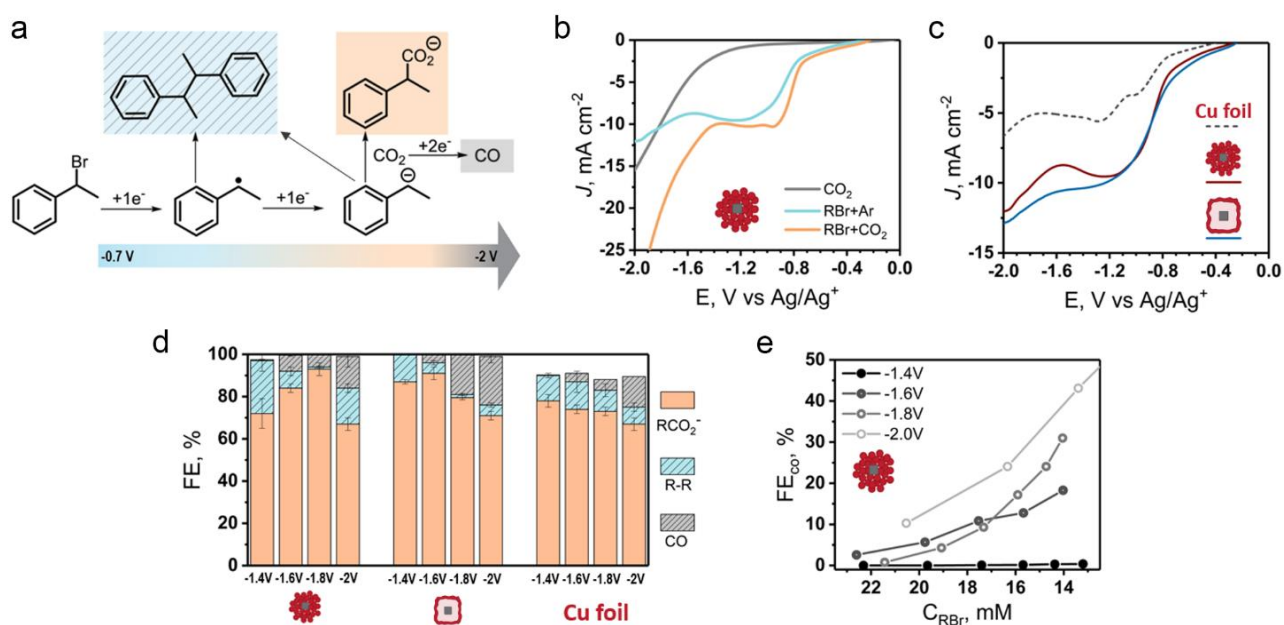


Figure 5. 26: Performance of raspberry-like NPs and Cu cages as cathodic materials for electrocarboxylation of (1-bromoethyl)benzene. (a) Shortened potential-guided mechanism of organohalide reduction in the presence of CO₂ with highlighted side reactions of homocoupling (light blue) and direct CO₂ reduction (grey). (b) Cathodic sweeps of CV recorded at 150 mV s⁻¹ at RL NP electrode in in CO₂ saturated ACN + 0.1 M TBAI (grey trace); in Ar saturated ACN + 25 mM (1-bromoethyl)benzene + 0.1 M TBAI (blue trace); and in CO₂ saturated ACN + 25 mM (1-bromoethyl)benzene + 0.1 M TBAI (orange trace); (c) Cathodic sweeps of CV recorded at 150 mV s⁻¹ in Ar saturated ACN + 25 mM (1-bromoethyl)benzene + 0.1 M TBAI at polished Cu foil (dashed black trace), raspberry-like NPs (red trace), and cages (blue trace). (d) Total FEs of major electrolysis products: RCO₂⁻, (orange), R-R (light blue) and CO (grey) after passing a charge of 1 F mol⁻¹ during potentiostatic electrolysis of (1-bromoethyl)benzene at different potentials using RL NPs and CGs as well as Cu foil as cathodic materials. (e) FEs of CO as a function of (1-bromoethyl)benzene concentration at different applied potentials.

observed for RBr reduction in Ar-saturated electrolyte that correspond to the first (at -1 V) and second (at -1.28 V) electron transfers. For both tested Cu NPs these two peaks overlapped, indicating facilitated second electron transfer. Cu NPs showed a higher geometric current density for RBr reduction than that of Cu foil. The onset and peak potentials were similar for both studied nanostructures.

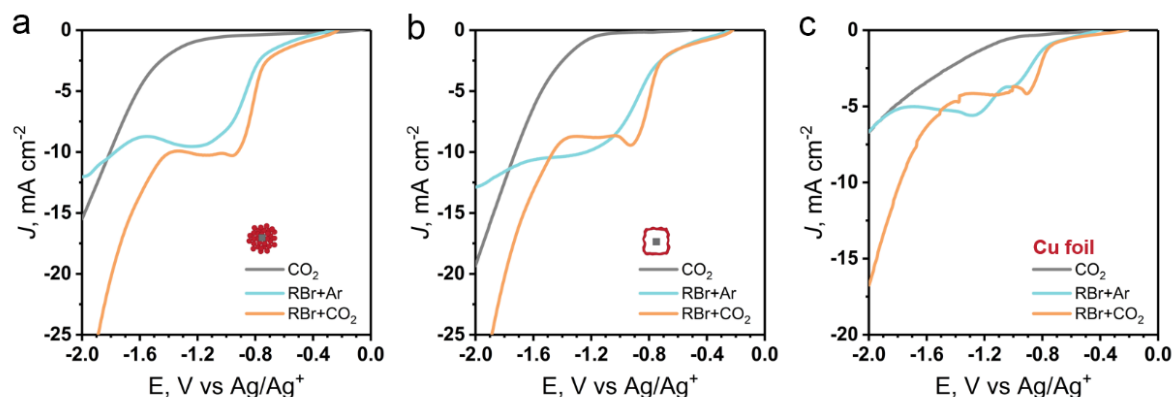


Figure 5. 27: Cathodic sweeps of cyclic voltammograms recorded in CO_2 -saturated 0.1 M TBAI in CH_3CN (grey traces), in Ar-saturated 0.1 M TBAI and 25 mM (1-bromoethyl)benzene solution in CH_3CN (blue traces), and in CO_2 -saturated 0.1 M TBAI and 25 mM (1-bromoethyl)benzene solution in CH_3CN (blue traces) at 150 mV s^{-1} scan rate at raspberry-like Cu NPs (a), Cu cages (b), and Cu foil (c).

The potentiostatic electrolysis was performed in a divided cell separated by an AEM. We conducted the electrolysis at more negative potentials than the second electron transfer peak to minimize the formation of the dimer. Figure 5.26d shows FEs of observed products as a function of the applied potential and cathode material after 1 F mol^{-1} of electrons was passed. When Cu foil was used as a cathode, the total FE of carboxylate, dimer, and carbon monoxide was $< 91\%$, with the remaining charge consumed towards the formation of by-products, such as styrene and its oligomers, as confirmed by NMR analysis of the crude mixture.⁷⁶ In the case of the nanostructured electrodes, only the formation of RCO_2^- , R-R, and CO was observed, accounting for approximately 100% FE. The carboxylate FEs were up to 93% for raspberry-like NPs and cages, whereas the highest FE for the foil was only $\sim 78\%$. At $-1.4 \text{ V vs Ag/Ag}^+$ the contribution of radical coupling was high with FE of R-R being $\sim 25\%$ for raspberry-like NPs and $\sim 13\%$ for cages. At more negative applied potentials the formation of R-R decreased to $\sim 1\%$ for both Cu NPs at $-1.8 \text{ V vs Ag/Ag}^+$; at -2 V vs Ag/Ag^+ FE of R-R rose for both NPs due to the increase in the current density that led to the drop in $[\text{CO}_2]:[\text{R}^-]$ concentrations ratio in the vicinity of the electrode. To assess the contribution of the side CO_2 electroreduction, we determined FEs of CO every 20 minutes during EC (Figure 5.26e). With the depletion of RBr in a course of electrolysis, the FE of CO increased. After passing the charge of 1 F mol^{-1} at -2.0 V , -1.8 V , and $-1.6 \text{ V vs Ag/Ag}^+$ FEs of CO reached

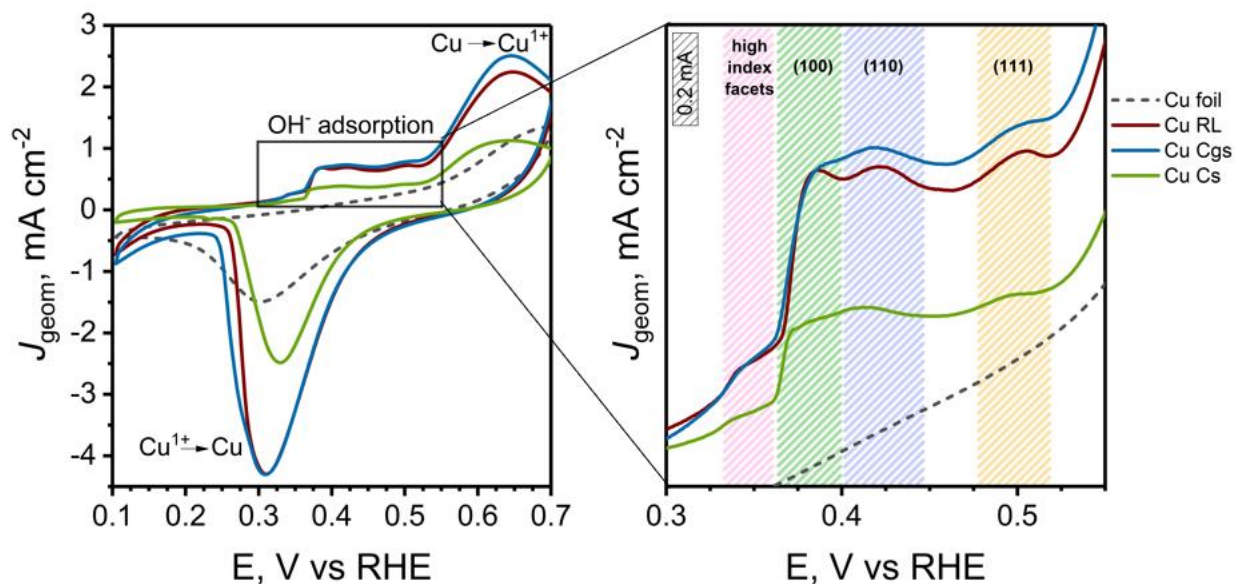


Figure 5. 28: OH^- adsorption CV curves obtained for Cu foil, Cu raspberry-like NPs, Cu cages, and Cu cubes in 0.1 M KOH at 100 mV s^{-1} scan rate.

~40%, ~30%, and 20%, respectively. In contrast, when a less negative potential of -1.4 V vs Ag/Ag^+ was applied FEs of CO remained low (<0.5%) in the course of the reaction.

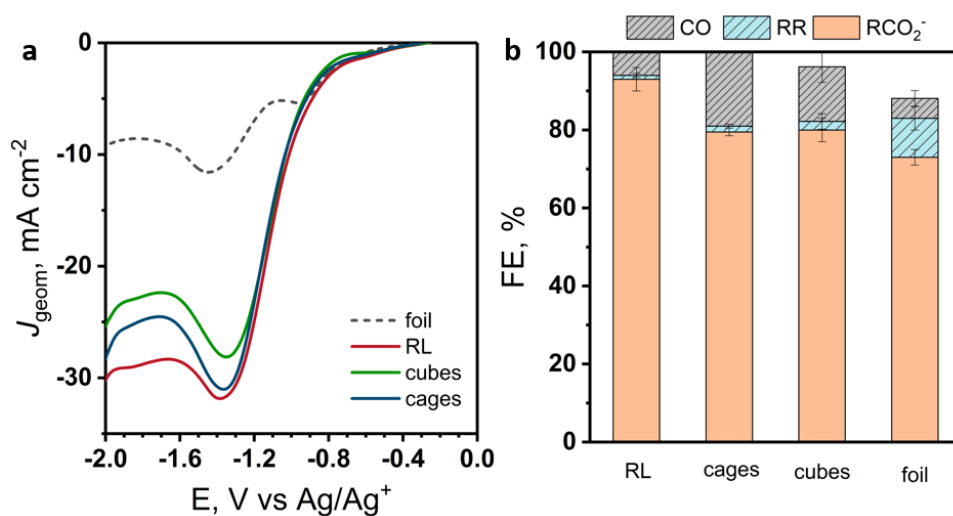


Figure 5. 29: Comparison of Cu NCs performance in EC of (1-bromoethyl)benzene to Cu RL NPs, Cu CGs, and Cu foil. CV curves obtained in Ar-saturated 0.1 M TEABF₄ with 100 mM (1-bromoethyl)benzene at a scan rate of 20 mV s^{-1} (a) and product distribution after the EC of 25 mM (1-bromoethyl)benzene in CO_2 -saturated 0.1 M TBAB solution in ACN at -1.8 V vs Ag/Ag^+ with a charge of 1 F mol^{-1} passed.

Cu NPs showed the highest FEs of carboxylate at -1.8 V vs Ag/Ag⁺ for Cu raspberry-like NPs and at -1.6 V vs Ag/Ag⁺ for Cu cages. At lower applied potentials the side reaction of radical coupling took place as energetically the second electron transfer was unfavorable. At higher applied potentials the contribution of the side CO₂ electroreduction increased. Notably, in the studied potential range no other products were detected. Overall, tested Cu NPs were superior to Cu foil, which showed low current densities, moderate FEs of carboxylate, and the formation of oligomeric by-products at all studied potentials.

As both Cu raspberry-like NPs and cages showed great performance in EC, we compared their performance to Cu NPs with more conventional cubic shape. First, we performed OH⁻ adsorption to determine the exposed NP surface morphology as well as assess electrochemically active surface area (ECSA) of the prepared electrodes. (Figure 5.28) We have not noticed any drastic difference in the NP surface morphology but observed lower OH⁻ adsorption currents for Cu NCs compared to Cu RL and Cu CGs which hinted at a lower ECSA. To further compare ECSA of these electrodes we performed Pb_{UPD} (Figure 5.29). Interestingly, all studied Cu nanomaterials showed relatively close Pb_{UPD} charge, which indicated that their ECSA was very close and all significant differences in activity should be attributed solely to their difference in surface morphology. Finally, we tested Cu NCs performance in the EC of (1-bromoethyl)benzene. (Figure

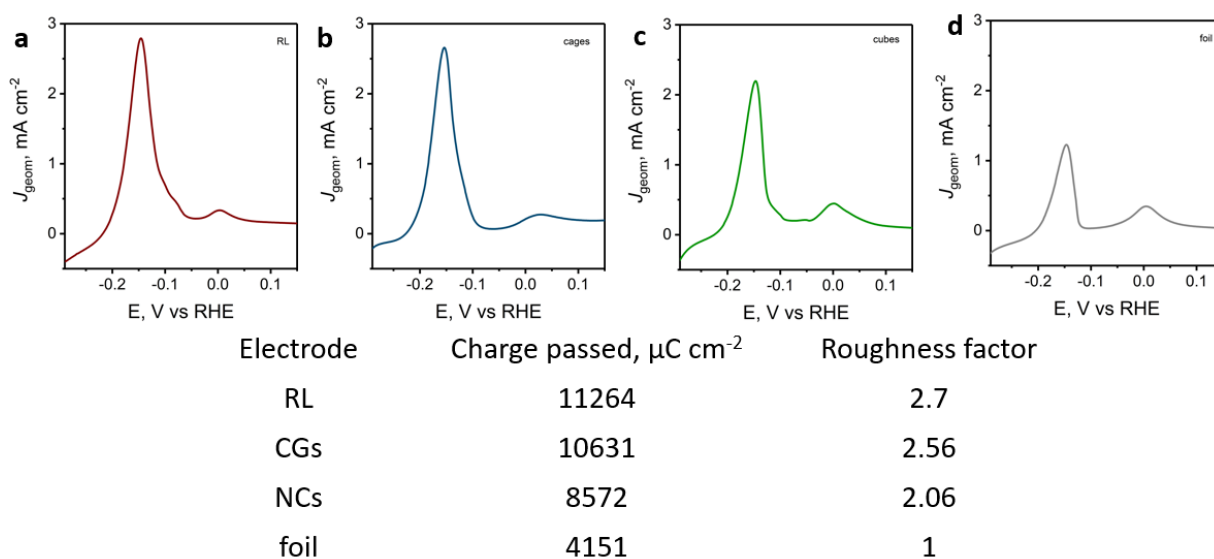


Figure 5. 30: Stripping curves of lead underpotential deposition on studied Cu electrodes. Baseline subtracted Pb_{UPD} stripping LSVs for RL (a), CGs(b), NCs (c), and foil (d) with roughness factor calculations. Performed in Ar saturated 100 mM HClO₄ aqueous solution with 1 mM Pb(ClO₄)₂ at a scan rate of 20 mV s⁻¹ in a potential range from 0.256 to -0.294 V vs RHE.

5.30) The activity of tested electrodes decreases in a row RL>CGs>NCs>foil based on the performed LSVs of the (1-bromoethyl)benzene in the absence of CO₂ (Figure 5.30a). For the studied series of Cu NPs, the difference in activity was comparable to the difference in the ECSA calculated from the Pb_{UPD}. However, when we performed potentiostatic electrolysis at arbitrary potential of -1.8 V vs Ag/Ag⁺, we have noticed that Cu NCs showed noticeably worse performance compared to Cu RL NPs and Cu CGs with about 5% of unaccounted FE that went towards the oligomerization of organohalide. Thus, not all studied Cu NPs have a similar superior performance. Considering that the surface of RL NPs and CGs was quite similar (Figure 5.16 and 5.23), their greater performance than that of NCs suggests that the reacting molecules may not be entering the inner space of the cages, but the high degree of the surface development is important for the active and selective EC.

Lastly, we performed a stability study on the Cu RL NPs using SEM. Figure 5.31 shows the degradation of Cu RL NPs after 3 rounds of EC at -1.8 V vs Ag/Ag⁺. It is important to note that the electrode was exposed to oxygen in between the reactions which could have been the reason

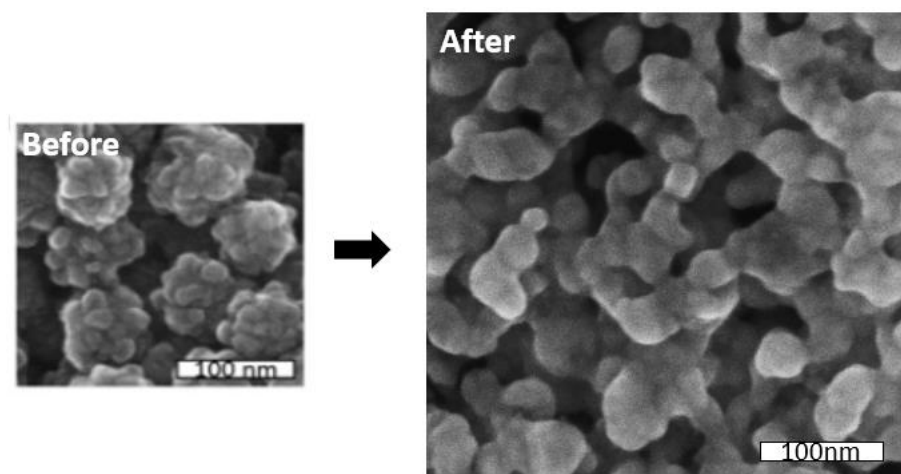


Figure 5. 31: Cu RL NPs stability after three EC reactions at -1.8 V vs Ag/Ag⁺. SEM images of the Cu NPs before and after electrolyses.

for the surface oxidation-reduction cycles that influenced the surface deconstruction along with the adsorbed reaction intermediate-induced atomic mobility that occurred during the EC itself.

5.4 Pd NPs for the EC of imines

The EC of N-benzylideneaniline on bulk electrodes discussed in Chapter 4 showed good results on many studied materials with the selectivity towards carboxylate of up to 95.5%. However, higher selectivity was associated with the lower material activity. We were curious whether we can significantly improve the catalyst selectivity of materials with higher activity by replacing a polycrystalline foil with NPs of various morphologies. We chose Pd with FE towards carboxylate of only 60% as our material of interest. We compared the performance of the bulk Pd material to Pd BNPs (Figure 5.32a) rich with high index facets and Pd NCs (Figure 5.32b) enclosed with 100 facet. It is important to note that palladium nanoparticles previously showed exceptional stability in cathodic transformations²⁸⁶ unlike many other metals, such as Ag, Au, and Cu.^{286,287}

The reactions were performed for NPs and Pd foil at three arbitrary potentials: -1.5 V, -1.75 V and -2 V. The results are summarized in Figure 5.32. In the case of Pd foil, the FE of EC increased from 60% at -1.5 V to 91.5% at -2 V, and the selectivity of imine reduction gradually increased from 70.5% at -1.5 V to 98% at -2 V due to the higher contribution of the mechanistic pathway *via* the activation of CO₂.

In contrast to Pd foil, both nanostructured materials showed significantly better performance at all studied potentials with FE of EC above 90% (Figure 5.33). The best results were achieved at -2 V with 100% selectivity of imine reduction and electrocarboxylation FE of up to 94%. Notably, both Pd NCs and Pd BNPs also showed much greater performance at -1.5 V with

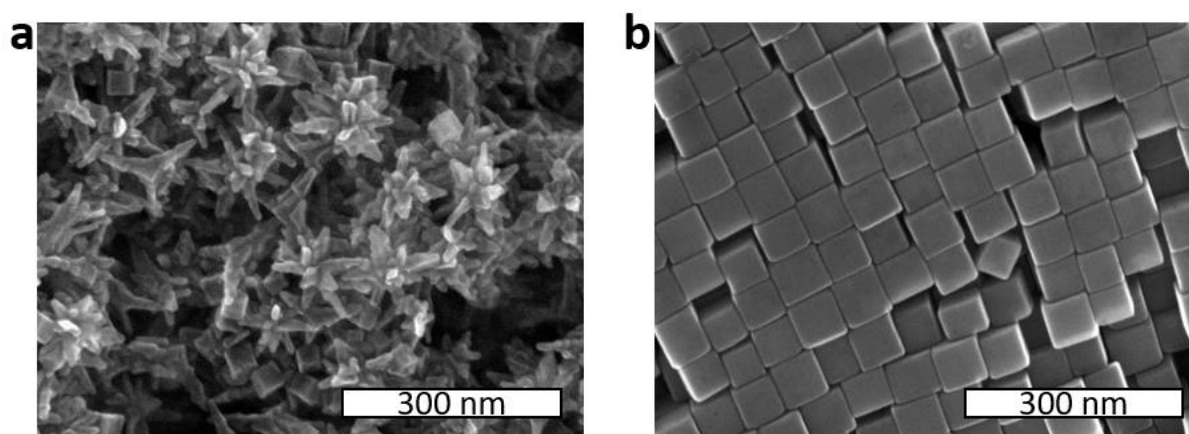


Figure 5. 32: Pd NPs used as electrocatalysts for the EC of N-benzylideneaniline obtained via seed-mediated synthesis in aqueous solutions of cationic surfactants: Pd BNPs (a) and Pd NCs (b).

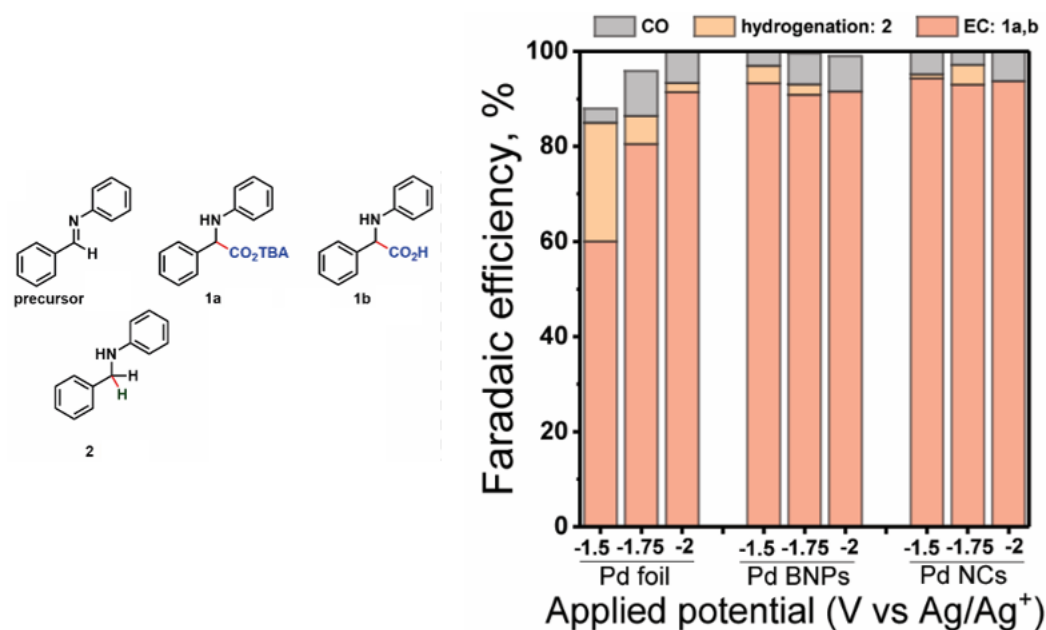


Figure 5. 33: The performance of nanostructured materials in EC of imines: FE of the major products as a function of applied potential and catalyst surface morphology.

1.5 times higher FE of EC compared to that of bulk Pd foil. In addition to the better efficiency of

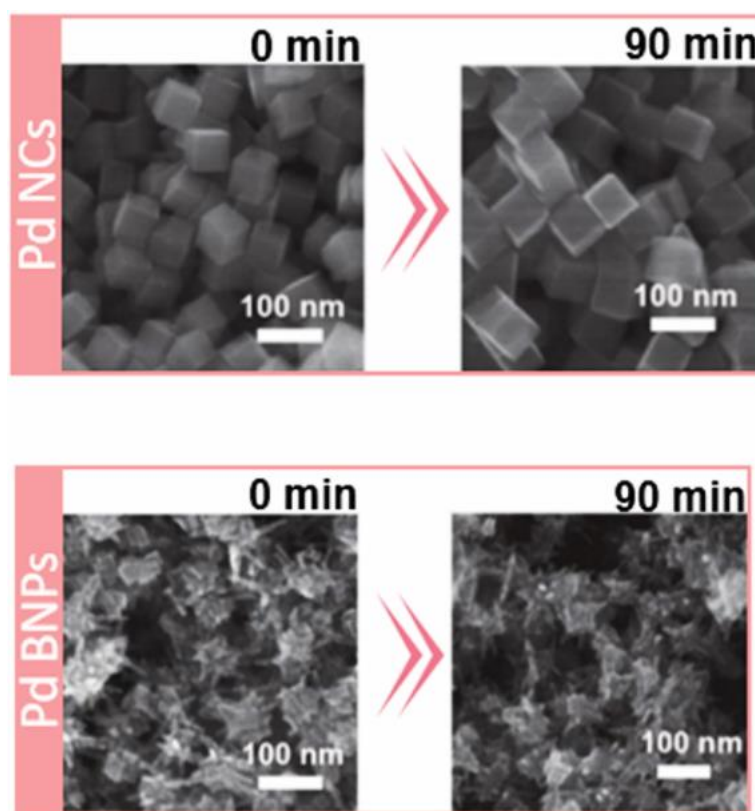


Figure 5. 334: The stability of Pd NPs after 90 min of EC.

EC on Pd NPs, the reactions had higher geometric current densities compared to Pd foil. To elucidate the stability of Pd nanoparticles in the EC of imines at the nanoscale level, we analyzed the electrodes before and after the reaction by SEM. No noticeable changes were observed for both Pd NCs and Pd BNPs (Figure 5.34). Due to the high stability and improved selectivity of Pd nanoparticles compared to that of Pd foil, Pd NCs and BNPs can be considered as promising cathode materials for the EC of imines. Further studies of the performance of different nanostructures made of cheaper metals could be also of high interest, including the studies on the EC of the imines bearing substituents with different electronic properties.

5.5 Summary

In this Chapter I studied the performance of metal NPs in EC of organic halides and imines. I found that the nature of the material as well as NP surface chemistry and morphology synergistically play a crucial role in the EC outcome.

First, I showed that metal nanoparticles synthesized in aqueous solutions of cationic surfactant are great electrocatalyst candidates for EC. Formed NPs are stabilized by a micellar double layer and these surface functions can be easily stripped and the resulting metal surface is more selective towards EC and not CO₂ electroreduction unlike citrate-stabilized NPs.

Second, I showed that NPs outperform bulk materials of the same nature in both activity and selectivity of the EC of organohalides and imines. I demonstrated that although all tested Cu NPs showed greater performance in the EC of organohalides compared to Au NPs, their stability was significantly worse than that for Au NPs. Also, I found that the presence of features that induce electrochemical activity, such as hot spots, decrease the EC of organohalide selectivity due to their unproportional enhancement of the competing CO₂ electroreduction. Additionally, I showed that for the EC of imines Pd NPs with extrusions as well as simple NCs both showed elevated and similar performance regardless their surface morphology and specific shape features. Moreover, both types of Pd NPs showed no structural changes during the EC of imines.

Chapter 6 Cell design optimization for EC: pressure cell

6.1 Introduction

As demonstrated in Chapter 3 and 5, the EC selectivity is the function of $[\text{CO}_2]/[\text{R-Hal}]$ ratio in the vicinity of the electrode and it drops significantly with the decrease of this ratio. Specifically, I showed that Ag-catalyzed electrocarboxylation of (1-bromoethyl)benzene in CO_2 -saturated ACN yields target carboxylic acid with almost quantitative yield only in very diluted solutions, whilst yield drops to 20% for 0.1 M solution of organohalide. This decrease is associated with the higher probability of the catholically formed carbanion reaction with the initial organohalide rather than that with CO_2 because of the small concentration of the latter in the vicinity of the electrode. To overcome this problem, the concentration of CO_2 in the solution should be increased, which can be achieved either by decreasing the temperature or by increasing CO_2 pressure. I showed that EC under reduced temperature can proceed with twice higher EC yield compared to room temperature, but yield remained low for $[\text{RBr}] \geq 0.05 \text{ M}$. For synthetic applications, however, the EC should be optimized so that high FE of EC can be achieved for more concentrated solutions. Further optimization can be achieved *via* the use of pressurized reactors, supercritical CO_2 , and ionic liquids (ILs) with high CO_2 solubility. In the Chapters 4 and 5, I demonstrated that the EC selectivity is also a function of cathode material nature, thus, the usage of the right electrocatalyst in synergy with the increased CO_2 concentration is a promising path towards the optimized EC at high precursor concentrations.

A several studies attempted the EC in pressurized systems for different types of organic compounds, including organohalides, ketones, alkenes and dienes.³¹²⁻³¹⁹ The results of these studies are summarised in Table 6.1. The increase of CO_2 pressure positively affected the reaction selectivity in all cases, resulting in the moderate to high yields of corresponding carboxylic acids. It has been demonstrated that pressurised systems were suitable for initial organic precursor concentrations ranging from 0.1 M to 0.5 M, whilst the EC for concentrated solutions (e.g., 8 M) failed to produce noticeable amount of target product. Notably, the least satisfying results were achieved for EC of organohalides: 47% for 0.1 M organic precursor solution, and only 20% for 0.4 M. Moreover, all studies were performed in undivided cells with sacrificial metal anodes. Thus, a lot of challenges are left for the further development of EC in pressurised systems.

Table 6. 1: The summary of studies on EC in undivided cells with CO₂ concentration higher than that for ambient conditions.

CO ₂ delivery method	Cathode/Anode	Precursor	Electrolyte	<i>E</i> or <i>J</i>	Yield (%)	Ref.
Gas (5 atm)	Zn / GC	0.15 M Ph ₂ CHOH ¹	TEAAc, ACN	7 mA cm ⁻²	61	312
Gas (1 MPa)	Stainless steel / Mg	0.1 M PhCH ₂ Cl	TBAP, DMF	30 mA cm ⁻²	34 ²	313
Gas (6 MPa)	Stainless steel / Mg	0.1 M PhCH ₂ Cl	TBAP, DMF	30 mA cm ⁻²	47 ²	313
ScCO ₂ (9 MPa)	Stainless steel / Mg	8 M PhCH ₂ Cl	TDATPhB ³	75 mA cm ⁻²	0.3 ⁴	313
Gas (1 MPa)	Ni / Al	0.2 M butadiene	TBABr, DMF	10 mA cm ⁻²	65	314
Gas (3 MPa)	Ni / Al	0.2 M butadiene	TBABr, DMF	10 mA cm ⁻²	84	314
Gas (0.1 MPa)	Pt / Al	0.4 M PhMeCHCl	[DEME][TFSI] ⁵	2 mA cm ⁻²	32	315
ScCO ₂ (10 MPa)	Pt / Al	0.4 M PhMeCHCl	[DEME][TFSI]	2 mA cm ⁻²	60	315
Gas (4 MPa)	Ni / Al	0.1 M acetophenone	TBABr, DMF	10 mA cm ⁻²	84	316
Gas (5 bar)	Ni / Al	0.2 M cyclohexadiene ⁶	TBABr, DMF	10 mA cm ⁻²	96	317
Gas (20 bar)	Ni / Al	0.2 M cyclohexadiene ⁶	TBABr, DMF	10 mA cm ⁻²	57	317
Gas (0.1 MPa)	Ni / Al	0.12 M styrene	TBABr, DMF	5 mA cm ⁻²	76	318
Gas (4 MPa)	Ni / Al	0.12 M styrene	TBABr, DMF	5 mA cm ⁻²	86	318
Gas (4 MPa)	Ni / Al	0.5 M styrene	TBABr, DMF	25 mA cm ⁻²	75	318
Gas (0.1 MPa)	Pt / Mg	0.4 M PhMeCHCl	DEME-TFSA ⁷	-2.5 V vs. Pt	5.5	319
Gas (3 MPa)	Pt / Mg	0.4 M PhMeCHCl	DEME-TFSA	-2.5 V vs. Pt	20	319

¹Precursor undergoes oxidation at GC anode to form corresponding ketone, which then participates in EC reaction. ²Yield was calculated based on the conversion of precursor and reaction selectivity provided in original manuscript. ³Tetrakis(decyl)ammonium tetraphenylborate. ⁴Most of the current went to competing CO₂ electroreduction. EC selectivity was 73%. ⁵N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl) imide. ⁶1,3-cyclohexadiene. ⁷N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis-(tri-fluoromethanesulfonyl)amide

In this chapter, I explore the EC of organohalides in specially designed and fabricated divided electrochemical cell that can operate under high CO₂ pressure (up to hundreds psi). I show that this system configuration allows to obtain moderate to quantitative FEs of EC for a wide range of organohalide concentrations (up to 0.2 M). I show that increase in the pressure of CO₂ not only leads to significant improvement of reaction selectivity, but also enables the suppression of undesirable electrochemical dimerization of organohalide. Finally, I present a heat map showing

the dependence of FE of EC on both organohalide concentration and CO₂ pressure, which can be used to predict pressure of CO₂ required to achieve a specific FE of target carboxylic acid.

6.2 Design of divided pressurised electrochemical cell for EC

As discussed in the Chapter 3, divided cells equipped with AEM are promising systems for sustainable EC paired with various useful anodic reactions in aqueous media, such as UOR and AOR. The major drawback of these systems is narrow range of organic precursor concentrations when the FE of EC is high (usually, < 0.05 M). To overcome this problem, we designed pressurised divided system (Figure 6.1a-c) capable of the precise tuning of $[\text{CO}_2]/[\text{R-Br}]$ ratio by varying the CO_2 pressure (Figure 6.1d).

First, we designed and fabricated an electrochemical cell comprising of pressure gauge, electrode holders, Ag wire quasi-reference electrode, and AEM. Cathodic and anodic

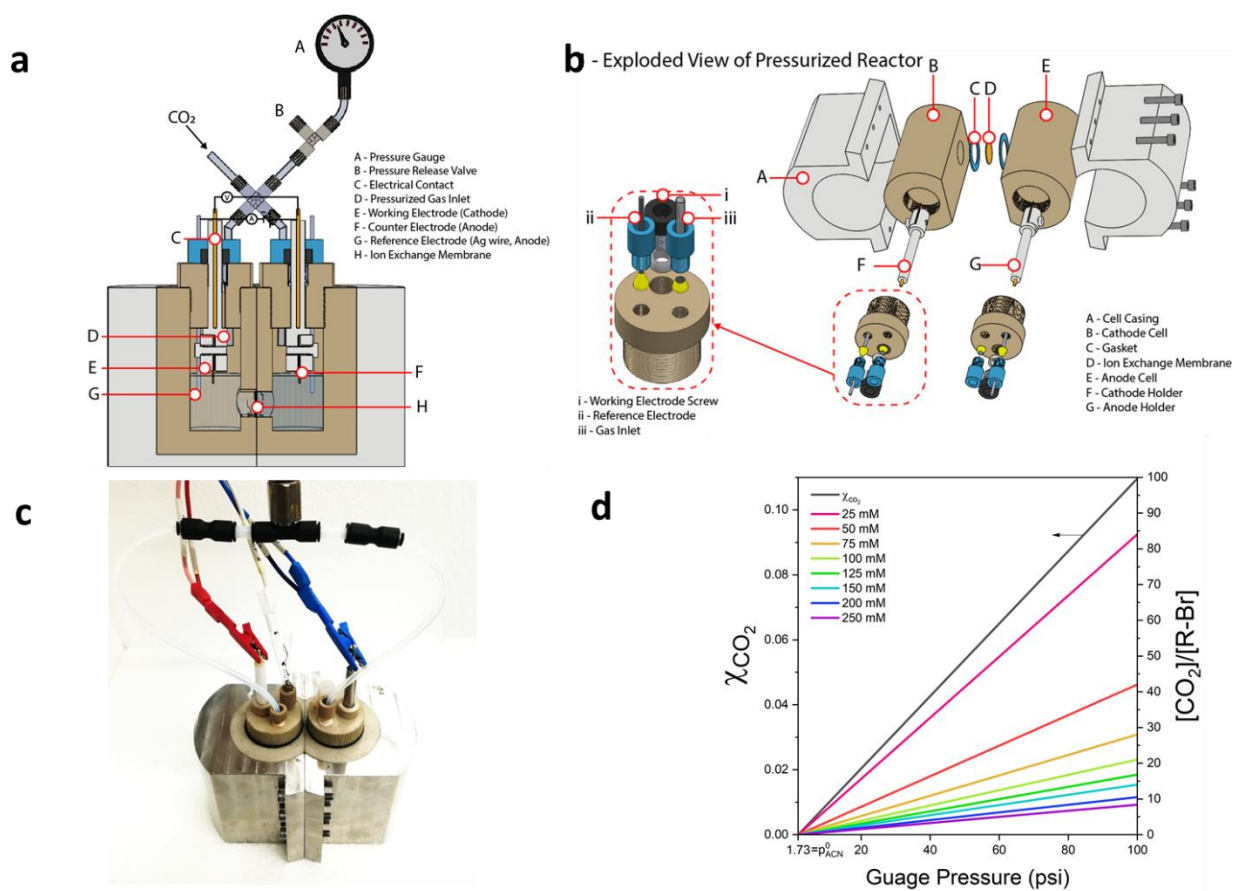


Figure 6. 1: Cross-section view (a) and exploded view (b) CAD rendered images of the cell vs. photo of the assembled cell (c). (d) Calculated mole fraction of CO_2 in ACN as a function of pressure (left-hand axis) and relative concentration of CO_2 to R-Br for different concentrations of substrate (right-hand axis)

compartments as well as caps were made from polyetheretherketone (PEEK),³²⁰ which was chosen due to its high stability under harsh environments, high elastic modulus (3.6 GPa), and excellent dimensional stability. Chemical-resistant gaskets and Viton O-rings were used for the sealing of the cell. In addition, a steel jacket was introduced around cathodic and anodic compartments for an additional sealing and safety precautions. Ag wire was sealed it with an epoxy resin.

The pressure system comprises of a CO₂ gas source, pressure regulator, pressure vessel, and digital barometer with an exhaust valve. Compressed CO₂ gas cylinder equipped with a pressure regulator was used as a CO₂ gas source. To prevent the deformation of the membrane due to the pressure gradient, CO₂ was supplied to both anodic and cathodic chambers with an equal pressure using a T-joint. Initial tests of the system showed that the pressurised cell can hold pressures up to hundreds psi with no signs of leakage.

The specificity of the cell design brings some limitations to the anodic reaction choice. Specifically, as both compartments headspaces have high pressure of carbon dioxide, the pH of solutions can not be very alkaline (< 11) to eliminate the acidification of the anolyte due to the reaction between carbon dioxide and excess hydroxide ions in electrolyte. Here, for simplicity, we chose the oxidation of electrolyte (TBAI in ACN) as anodic process, but alternative anodic reactions such as OER or AOR can be considered in the future.

6.3 The electrochemical studies of EC of benzyl bromide in divided pressurised electrochemical cell

6.3.1 Competing CO₂ electroreduction in pressurised cell

As demonstrated in Chapter 4, polycrystalline bulk Cu shows great performance in the EC of organohalides and was used in this work as an arbitrary cathode. Generally, the activation of organohalide requires a lower energy input than that of CO₂, so we set to determine the potential window where the CO₂ activation does not occur, and one can perform EC without the competing CO₂ electroreduction. This is especially important for pressurised systems, where FE of undesirable CO₂ electroreduction would significantly increase with increasing pressure of CO₂. To this end, we investigated the electrochemical behavior of CO₂ at Cu cathode at different pressures of CO₂ (Figure 6.2). The onset potentials for CO₂ were around -1.4 V vs Ag/Ag⁺ for all tested pressures (0-80 psi), and the current density of CO₂ electroreduction increased noticeably from 25 mA cm⁻² at ambient pressure to 45 mA cm⁻² at 80 psi. Low to no CO₂ electroreduction activity was observed for $E > -1.5$ V vs Ag/Ag⁺, making them optimal for the efficient EC *via* R-Hal activation with the minor contribution of competing CO₂ electroreduction.

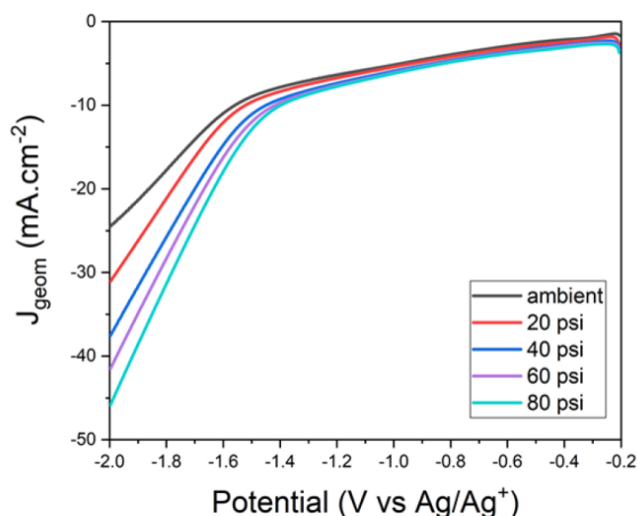


Figure 6. 2: Linear sweep voltammograms recorded at 100 mV s⁻¹ scan rate at Cu cathode for CO₂-saturated electrolyte at different CO₂ pressures.

6.3.2 EC in pressurised cell

In agreement with the results discussed in Chapter 4, the onset potential of (1-bromoethyl)benzene reduction at Cu cathode was about -0.8 V vs Ag/Ag⁺ and two distinct peaks were observed at about -1.0 V vs Ag/Ag⁺ and -1.3 V vs Ag/Ag⁺. These peaks correspond to the one-electron reductive cleavage of the C-Br bond with the formation of radical specie and subsequent reduction of the radical to the corresponding carbanion. We note that the curve for

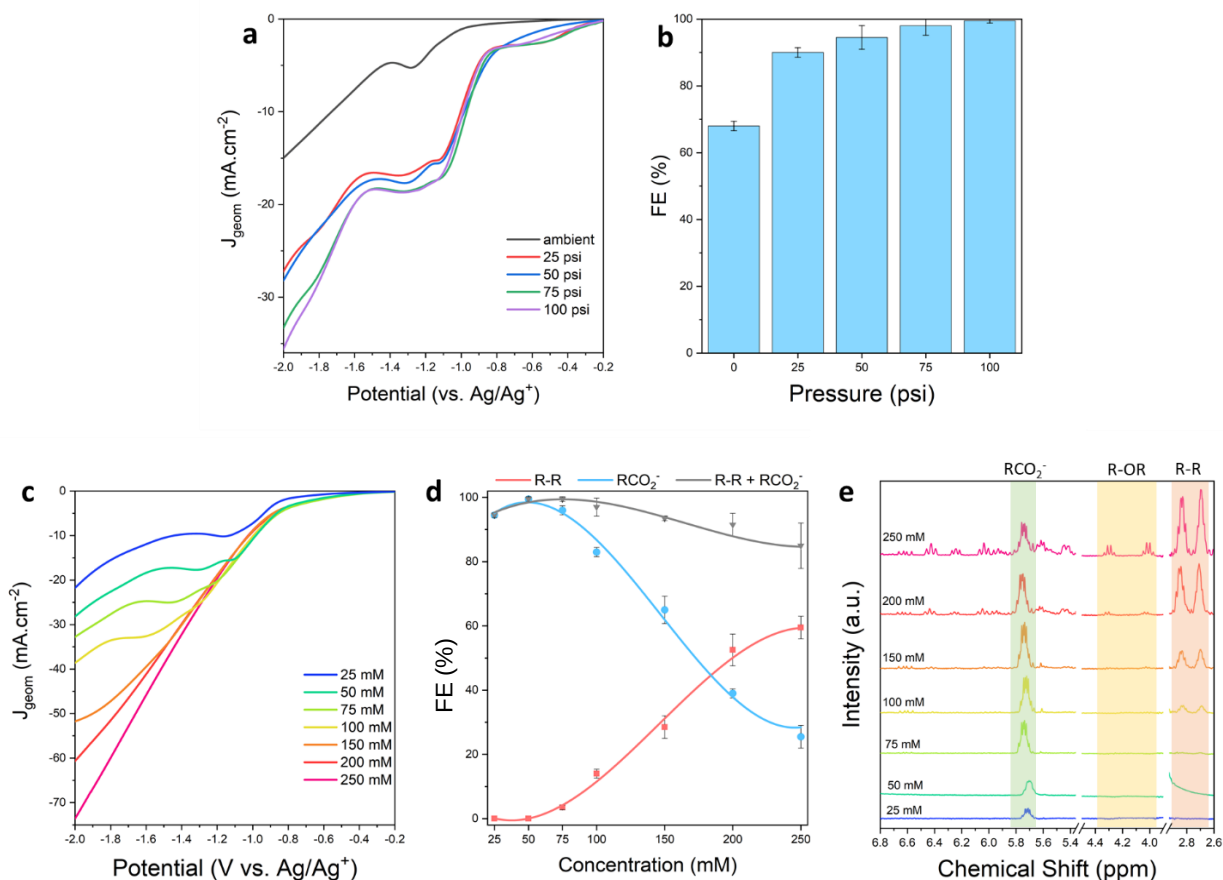


Figure 6. 3: Effect of CO₂ pressure on EC outcome. (a) LSV recorded at 100 mV s⁻¹ at Cu cathode for 0.05 M (1-bromoethyl)benzene solution in CO₂-saturated electrolyte at different CO₂ pressures. (b) The FE of EC performed at -1.4 V vs. Ag/Ag⁺ after passing charge of 0.5 F mol⁻¹ as a function of CO₂ pressure. (c) LSV recorded at 100 mV s⁻¹ at Cu cathode for different concentrations (0.025 – 0.25 M) of (1-bromoethyl)benzene in CO₂-saturated electrolyte at fixed pressure of 100 psi. (d,e) The major products distribution and ¹H-NMR spectra of crude reaction mixtures for the potentiostatic EC of (1-bromoethyl)benzene performed at -1.4 V vs. Ag/Ag⁺ and 100 psi CO₂ pressure after passing charge of 0.5 F mol⁻¹ as a function of organohalide concentration.

ambient pressure was different from the curves recorded at constant CO₂ pressure likely due to the lack of CO₂ in the solution. Only small changes were observed with increasing of CO₂ pressure from 25 psi to 100 psi. Considering this data and the data obtained for CO₂ electroreduction, the optimal potential window for EC in pressurised cell is between -1.3 V vs Ag/Ag⁺ and -1.5 V vs Ag/Ag⁺: these potentials are high enough to efficiently convert organohalide to corresponding carbanion and low enough to suppress competing CO₂ electroreduction. It was shown in Chapter 5 that at ambient CO₂ pressure (1-bromoethyl)benzene produces noticeable amounts of dimer at potentials below -1.6 V vs Ag/Ag⁺, thus, carboxylate/dimer ratios in the chosen potential range (-1.3 V to -1.5 V vs Ag/Ag⁺) would work as a clear indication of the cell efficiency.

Next, we performed the series of potentiostatic electrolyses of 0.05 M (1-bromoethyl)benzene at -1.4 V vs Ag/Ag⁺ varying CO₂ pressure (Figure 6.3b). The electrolysis at ambient pressure was performed with the constant delivery of CO₂ at a rate of 14 sccm resulting in the FE of carboxylate slightly below 70%, which was within error bars of the FE obtained in a conventional H-cell for the same reaction (see Chapter 5). Interestingly, the FE value increased dramatically with the increasing pressure of CO₂, reaching almost 100% at 100 psi. Since 100 psi pressure was found to be optimal for the electrolysis, we studied EC at this pressure for different concentrations of (1-bromoethyl)benzene (Figure 6.3c-d) at -1.4 V vs Ag/Ag⁺. We found that the FE of EC decreases with increasing organohalide concentration and reached about 30% for 0.25 M (1-bromoethyl)benzene. At the same time the FE of electrochemical dimerization proportionally increased with the increasing concentration of organohalide owing to the increasing probability of organohalide molecules residing in the vicinity of the electrode and, thus, being more readily available species for reacting with the electrogenerated carbanion. In addition, combined FE of carboxylate and dimer slightly decreased with increasing concentration of (1-bromoethyl)benzene, which can be associated with other side reactions of the carbanion and formation of different by-products, which were clearly seen on the NMR of crude reaction mixtures (Figure 6.3e). Almost linear relationship between the FE of carboxylate and organohalide concentration suggested that the further improvement of reaction selectivity should be performed by adjusting the CO₂ pressure.

To fully disentangle the carboxylate FE dependency on the organohalide concentration and CO₂ pressure, we performed multiple experiments for different concentrations of (1-bromoethyl)benzene at various CO₂ pressures and constructed a heat maps for the FE of

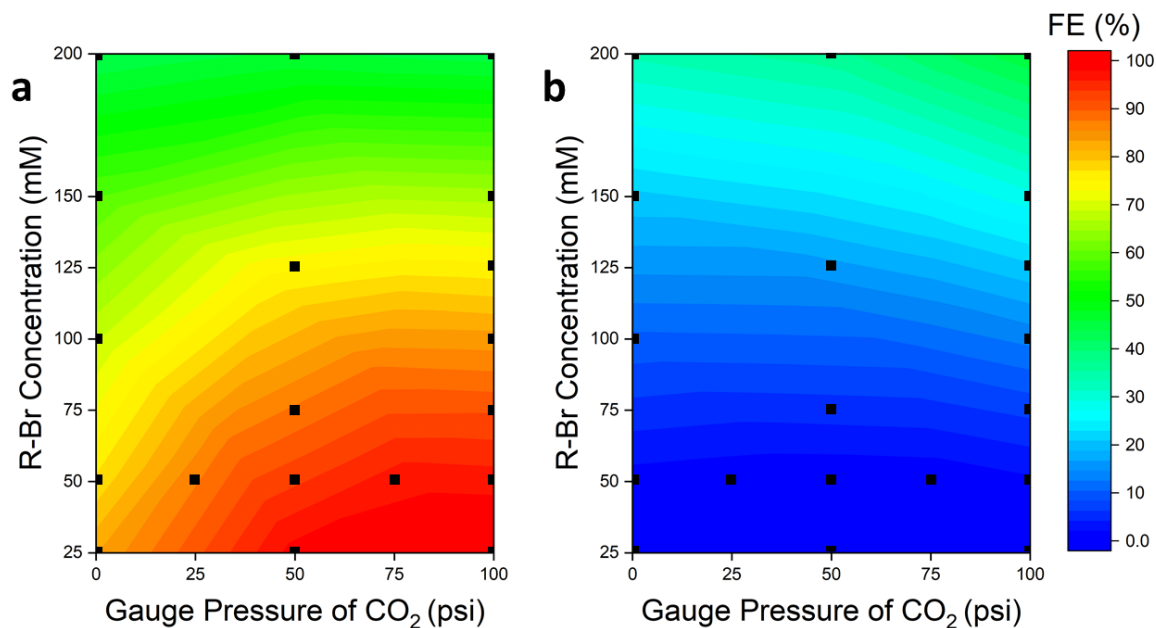


Figure 6. 4: Heat maps showing FE of carboxylate (a) and dimer (b) with respect to CO₂ pressure and R-Br concentration.

carboxylate and dimer as the function of organohalide concentration and CO₂ pressure (Figure 6.4). We found that, in general, the pressure of CO₂ should be increased for increasing organohalide concentration to achieve quantitative FE of EC. However, for highly concentrated solutions of (1-bromoethyl)benzene (e.g., 0.2 M) selectivity remains below 60-70% for all studied CO₂ pressures likely due to the mass transfer limitations.

Overall, the designed cell showed a good performance in the EC of (1-bromoethyl)benzene for the wide range of concentrations. Our pressurized system showed much better performance than that of a previously reported systems for the EC of organohalides. Yet, only moderate FEs (<70%) were achieved for very concentrated solution of organohalide and further optimization is required to achieve high selectivity of EC for these extreme concentrations.

6.4 Summary

In this chapter, I explored the performance of pressurised electrochemical cell for the EC of organohalides on the example of (1-bromoethyl)benzene. The cell was designed and fabricated to operate at moderate CO₂ pressures (hundreds psi). I demonstrated that [CO₂]/[R-Hal] ratio is responsible for the EC selectivity and that this ratio can be optimized by adjusting the CO₂ pressure. Up to quantitative FEs of the EC target product were achieved for a wide range of (1-bromoethyl)benzene concentrations (0 M < [R-Hal] < 0.2 M).

Chapter 7 Conclusions and Future Work

The work presented in this thesis focused on the optimization of the electrocarboxylation of organohalides and imines in divided electrochemical systems by implementing paired electrolysis and nanoscale catalysis. The overarching goal of this work was to transition from the conventional undivided electrochemical cells with sacrificial anodes to sustainable and scalable systems while maximizing their efficiency and clarifying the reaction mechanism.

First, in Chapter 3 this thesis demonstrated the principal feasibility of performing EC reactions in divided cells with aqueous anolytes and nonsacrificial anodes. Chapter 3 laid out the critical role of the membrane separator type and showed that AEM has a superior performance with the highest EC selectivity and the lowest cathode passivation, compared to those of CEM and BPM. For the AEM divided system, the reaction scope and limitations were explored, the optimal reaction conditions were determined, and the reaction mechanism in the absence of dissolved metal ions was proposed. Furthermore, Chapter 3 demonstrated that EC can be coupled with N-footprint mitigating anodic reactions such as UOR and AOR that simultaneously decrease the energy requirements of an electrolyzer.

Chapter 4 explored the impact of the nature of bulk metal electrocatalysts on the outcome of EC of organohalides and imines. Specific electrochemical properties of different metal electrodes were mapped including potentials zones for the efficient EC and the potential windows where the CO₂ electrochemical activation does not occur. Chapter 4 demonstrated that both the nature of a cathode material and the nature of an organic precursor significantly affect the outcome of the reduction process.

Chapter 5 elucidated the performance of metal nanomaterials as electrocatalysts for the EC of organohalides and imines and demonstrated the superior performance of nanostructured materials over polycrystalline bulk metals of the same nature. NPs showed lower onset potentials, higher current densities, and greater selectivity in EC compared to bulk metals, reaching in some cases quantitative Faradaic efficiencies of target carboxylates. Despite the superior performance of NPs, their structural degradation to some degree was observed during EC, which was especially pronounced for Cu and some shapes of Au NPs: complex core-cage nanostructures collapsed within a few hours, while other studied shapes underwent surface smoothing. Interestingly, Pd NPs demonstrated superior stability compared to both Cu and Au NPs. Also, Chapter 5 showed that in

addition to surface morphology, NP surface chemistry comprised of the adsorbed organic molecules plays an important role in the reaction outcome. It was shown that some capping agents (such as citrate) strongly bind to the NP surface and do not leave the surface even during reductive electrolysis under EC conditions, while others (e.g., cationic surfactants, such as CPC) are easily stripped from the surface making it more selective towards EC compared to the citrate-capped counterparts. The established trends in the NP performance in EC for the range of nanostructured materials with different nature as well as surface morphology and chemistry will help guiding the rational design of selective, active, and durable catalysts for EC.

In chapter 6 a pressurized divided cell was designed to study EC at high concentrations of organic precursors. The fabricated cell outperformed all previously reported systems for the EC of organohalides, allowing to achieve quantitative Faradaic efficiencies of carboxylate for the wide range of organic precursor concentrations. The results obtained in Chapter 6 enabled constructing a heat map of the EC FE dependence on both the organohalide concentration and the CO₂ pressure, which can be used to predict the pressure of CO₂ required to achieve a specific FE of target carboxylic acid.

This thesis explored the influence of the anodic reaction, separating membrane, applied potential, electrocatalyst, organic precursor concentration, and CO₂/organic precursor ratio on the cathodic EC of organohalides and imines in divided systems. The obtained results are seminal for the “new era” of EC: this thesis showed that avoiding the use of sacrificial metal anodes is possible and does not necessarily come at the price of the reaction selectivity or precursor concentration. The FEs of carboxylate were almost quantitative with the careful selection of the electrochemical system design, appropriate catalyst choice, and optimal reaction conditions, all of which were dictated by the trends and maps suggested in this thesis.

Further work on the transfer and optimization of the proposed EC approach into divided flow systems would open the door for continuous electroorganic CO₂ fixation giving a rise to industrially relevant carboxylic acids at practical potentials and currents. Considering the large scope of carboxylic acids that can be obtained *via* EC, it is important to perform the technoeconomic assessment and the life-cycle analysis to identify the most promising carboxylic acids that would benefit from this approach in terms of sustainability and cost.

In terms of the prospects of catalyst design studies, this work suggests that the beneficial for the EC use of nanoscale materials can be accompanied by their structural degradation. Thus,

all further studies should consider more reconstruction-resistant shapes (NSs, BNPs) without voids for metals with lower electrochemical stability (like Cu, Au), while there is no such limitation for metals with the high stability (such as Pd). Additionally, the map of electrocatalytic activity obtained in this work is a promising object for a further systematization using machine learning. This approach would identify the broader dependence of the electrocatalytic activity of metals on the organic precursor structure.

This thesis demonstrated that one can achieve high FEs of carboxylate at high organic precursor concentrations in the sacrificial anode-free divided batch reactors by increasing CO₂ concentration using pressure. Thus, the further optimization of the process design needs to connect the high concentrations of CO₂ in the vicinity of the electrode with the industrially relevant flow-through reactors for the EC. That can be achieved by implementing and optimizing the gas diffusion electrodes, which would enable the reaction to occur on a three-phase-interface of the solid electrocatalyst, CO₂ in a gas phase, and organic precursor dissolved in a liquid electrolyte.

To make the overall process more attractive, one can explore different value-added options for the paired electrolysis beyond AOR, UOR, and OER. For instance, useful concomitant anodic organic transformations that were not attainable in undivided systems.

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Electrochemical CO₂ Fixation to α -Methylbenzyl Bromide in Divided Cells with Nonsacrificial Anodes and Aqueous Anolytes

Author: Jury J. Medvedev, Xenia V. Medvedeva, Feng Li, et al

Publication: ACS Sustainable Chemistry & Engineering

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Date: Dec 1, 2019

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Translating Tactics from Direct CO₂ Electroreduction to Electroorganic Coupling Reactions with CO₂

Xenia V. Medvedeva, Jury J. Medvedev, Anna Klinkova 

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Relative activity of metal cathodes towards electroorganic coupling of CO₂ with benzylic halides

Author: Jury J. Medvedev, Xenia V. Medvedeva, Helen Engelhardt, Anna Klinkova

Publication: Electrochimica Acta

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Publication: Electrochimica Acta**Publisher:** Elsevier**Date:** 1 April 2005

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Electrode Materials in Modern Organic Electrochemistry

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Publication: Angewandte Chemie International Edition

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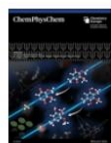
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Appendix

Calibration of Ag-wire (quasi-reference electrode)

The electrochemical measurements were conducted at ambient room temperature in a three-electrode cell. Pt wires were used as working and counter electrodes. A silver wire was used for a reference electrode. The measurements were performed in 5 mM ferrocene solution in 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄). Five scans were recorded at 100 mV s⁻¹ scan rate.

The half-wave potential ($E_{1/2}$) of the Fc⁺/Fc couple was determined according to the following equation: $E_{1/2} = E_{pa} - 1/2\Delta E_p$, where E_{pa} is the anodic peak potential, and ΔE_p is the anodic and cathodic peak separation (the difference between the anodic and cathodic peaks potentials).

The obtained potential ($E_{1/2} = 608$ mV vs Ag_{wire}) was compared with the literature data ($E_{1/2} = 454$ mV vs SCE; $E_{1/2} = 695$ mV vs SHE).

Thus, for the conversion of the potentials obtained using the Ag-wire to SHE or SCE, the following equations was used:

$$E(\text{recorded at SHE}) = E(\text{recorded at Ag-wire}) + 0.087 \text{ (V)}$$

$$E(\text{recorded at SCE}) = E(\text{recorded at Ag-wire}) - 0.154 \text{ (V)}$$

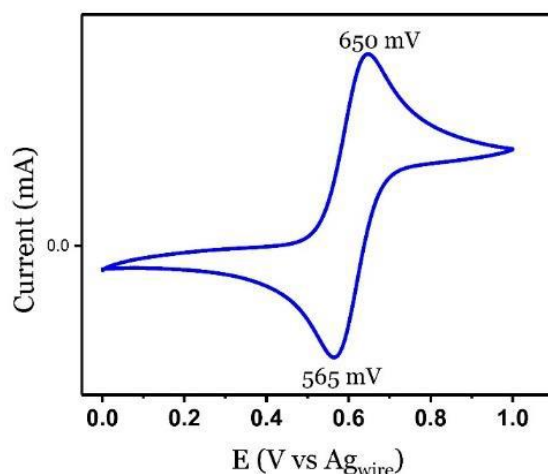


Figure A 1: CV of 5 mM ferrocene, recorded at scan rate 100 mV s⁻¹ at a platinum-wire electrode in 0.1 M TBABF₄ in ACN as supporting electrolyte.