Mechanistic Investigation of Electrochemical PET Degradation Using Diverse Electrode Materials: Identifying Optimized Conditions for Energy-Efficiency and Monomer Recovery

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Polyethylene terephthalate (PET), a widely used thermoplastic polymer, is difficult to recycle due to its stable chemical structure, and conventional methods such as mechanical and chemical recycling often lead to degraded material properties while being energy-intensive. Additionally, these methods are energy-intensive, requiring high temperatures and harsh reagents, which further reduce their sustainability. Current PET recycling methods, including mechanical and chemical approaches, suffer from low efficiency, high energy consumption, and limited monomer recovery. Electrochemical recycling presents a promising alternative, yet challenges such as catalyst stability, reaction scalability, and energy demands hinder widespread adoption. This study evaluates $CoNi_{0.25}P$ electrocatalysis and [N-DMBI] radical reduction, comparing their Faradaic efficiencies (>80%) and degradation pathways against conventional methods to determine their feasibility for large-scale PET recycling. Electrochemical degradation of PET offers a promising alternative, enabling selective breakdown into high-purity monomers with reduced energy consumption. This paper explores the key reaction intermediates and pathways involved in the electrochemical degradation of PET on various electrode surfaces, including platinum, carbon, and doped electrodes. This study evaluates the efficacy, scalability, and stability of electrochemical PET recycling using $CoNi_{0.25}P$ electrocatalysis and [N-DMBI] radical-mediated reduction, addressing key challenges such as catalyst degradation, energy consumption, and reaction efficiency. By systematically comparing these emerging techniques with traditional chemical recycling methods, this work highlights their potential for large-scale implementation, contributing to the development of more sustainable and economically viable plastic waste management solutions. As a review, this paper synthesizes existing research to identify trends and gaps in the field, providing a foundation for future investigations. By understanding these mechanisms, the review aims to contribute to a more sustainable approach to plastic waste management.

Introduction

The global plastic waste crisis has intensified the need for effective recycling technologies, particularly for polymers like polyethylene terephthalate (PET). PET is extensively used in packaging, textiles, and engineering applications due to its durability, transparency, and resistance to chemical degradation. However, these same properties make PET recycling challenging. Traditional recycling methods, such as mechanical recycling, often degrade the material's properties, while chemical recycling can be energy-intensive and complex. As environmental regulations tighten and the demand for sustainable materials grows, the development of efficient PET recycling methods is imperative[1].

Recent research in electrocatalytic and organocatalytic PET degradation has demonstrated potential for improving efficiency and sustainability, but there is a need to systematically compare these methods with conventional approaches. Studies in electrochemical catalysis and radical-driven depolymerization suggest that such techniques can offer improved monomer selectivity, lower processing temperatures, and reduced environmental impact, yet direct industrial applications remain limited. A key challenge is the lack of direct comparisons under standardized conditions, making it difficult to determine whether electrochemical approaches truly outperform established recycling processes. This study integrates insights from recent advancements in heterogeneous electrocatalysis, molecular electron donors, and chemical recycling to provide a comprehensive evaluation of PET degradation methods. Real-world applications demonstrating the viability of electrochemical PET recycling are discussed in Section 3, emphasizing how these emerging techniques could be optimized for large-scale implementation.

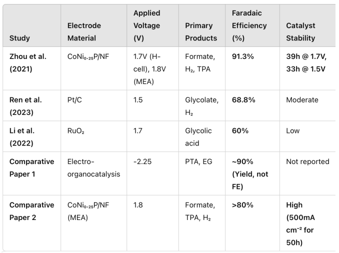
Polyethylene terephthalate (PET) accounts for > 70 million tons of global plastic production annually, yet current recycling rates remain below 20% due to the downgrading of mechanical recycling products and harsh conditions required for chemical depolymerization.[2]. Conventional techniques such as glycolysis and hydrolysis require high temperatures ($> 200°C$) and corrosive reagents, making them unsustainable for large-scale processing. Electrochemical PET degradation, using methods like $CoNi_{0.25}P$ electrocatalysis and electro-organocatalysis, offers a potential solution by operating under milder conditions and reducing energy input. However, critical challenges such as catalyst degradation, reaction efficiency, and monomer selectivity must be addressed before these methods can be industrially viable. This study aims to quantify the efficiency, scalability, and stability of electrochemical PET recycling methods to determine their potential for real-world implementation.

Both electrocatalytic PET degradation ($CoNi_{0.25}P$) and electro-organocatalytic PET depolymerization ([N-DMBI] radicals) present promising routes for sustainable plastic recycling, yet their efficiency, scalability, and real-world applications differ significantly. $CoNi_{0.25}P$ electrocatalysis, which primarily facilitates ethylene glycol oxidation to formate while producing hydrogen fuel, has demonstrated $>80\%$ Faradaic efficiency and high selectivity for formate. Its implementation in membrane-electrode assembly (MEA) reactors enhances current density up to 500 mA cm^{-2} at $\sim 1.8V$, making it more energy-efficient and scalable compared to conventional H-cell setups. This setup enables continuous operation, reducing Ohmic losses and enhancing ion transport, making it a viable candidate for industrial deployment in PET upcycling and hydrogen co-production.

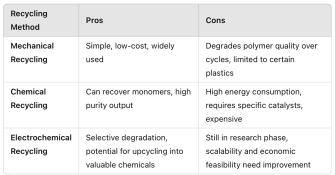
In contrast, electro-organocatalysis using [N-DMBI] radicals enables selective PET depolymerization, achieving $\sim 90\%$ monomer recovery (terephthalic acid and ethylene glycol) with Faradaic efficiencies exceeding 90%. The process operates under mild conditions ($-2.25V vs. Fc/Fc^+$ in acetonitrile), avoiding harsh reagents, making it a greener alternative to solvolysis and pyrolysis. Additionally, this method has been applied to glass-reinforced PET, a material typically resistant to conventional recycling techniques, demonstrating its versatility in handling complex waste streams. However, concerns remain regarding the stability and recyclability of [N-DMBI] radicals over multiple electrolysis cycles, which could limit large-scale adoption.

A direct industrial application demonstrating the superiority of electrocatalysis over conventional methods is seen in formate production from PET-derived ethylene glycol, where $CoNi_{0.25}P$ surpasses Pt/C and RuO_2 in selectivity and energy efficiency. Meanwhile, [N-DMBI] radical reduction offers a sustainable alternative for depolymerizing PET into its monomers, which is critical for circular plastic economy strategies.

Recent studies have demonstrated the potential of electrochemical methods for recycling polyethylene terephthalate (PET) waste into valuable products. For instance, Ma et al. reported the use of $NiCo_9S_8$ [3] nanosheet arrays grown on nickel foam as catalysts for the electrocatalytic reforming of ethylene glycol derived from PET. This approach achieved Faradaic efficiencies up to 92% for formate production, even when using commercial PET plastic powder hydrolysate, indicating its practical applicability.



Study	Electrode Material	Applied Voltage (V)	Primary Products	Faradaic Efficiency (%)	Catalyst Stability
Zhou et al. (2021)	$CoNi_{0.25}P/NF$	1.7V (H-cell), 1.8V (MEA)	Formate, H_2, TPA	**91.3%**	**39h @ 1.7V, 33h @ 1.5V**
Ren et al. (2023)	Pt/C	1.5	Glycolate, H_2	**68.8%**	Moderate
Li et al. (2022)	RuO_2	1.7	Glycolic acid	**60%**	Low
Comparative Paper 1	Electro-organocatalysis	-2.25	PTA, EG	**~90% (Yield, not FE)**	Not reported
Comparative Paper 2	$CoNi_{0.25}P/NF$ (MEA)	1.8	Formate, TPA, H_2	**>80%**	**High (500mA cm^{-2} for 50h)**



Recycling Method	Pros	Cons
Mechanical Recycling	Simple, low-cost, widely used	Degrades polymer quality over cycles, limited to certain plastics
Chemical Recycling	Can recover monomers, high purity output	High energy consumption, requires specific catalysts, expensive
Electrochemical Recycling	Selective degradation, potential for upcycling into valuable chemicals	Still in research phase, scalability and economic feasibility need improvement

Electrochemical degradation of PET has emerged as a promising alternative, offering several advantages over conventional methods. Electrochemical processes can operate at lower temperatures, reduce the need for harsh chemicals, and selectively target specific bonds within the polymer structure, leading to the recovery of high-purity monomers. Moreover, these processes can be integrated with renewable energy sources, further reducing the environmental impact. This research explores the key intermediates and reaction pathways involved in the electrochemical degradation of PET on different electrode surfaces, aiming to optimize the conditions for efficient recycling[4].

Summary of papers reviewed:

Table comparing different types of degradation:

Review Paper Selection Methodology:

To ensure a structured and unbiased analysis, a systematic approach was followed in selecting relevant literature for this review. Peer-reviewed journal articles and conference papers published in the past ten years were collected from databases such as Google Scholar, Scopus, Web of Science, and ScienceDirect. The search utilized the following terms: ”Electrochemical PET degradation,” ”Electrocatalysis for plastic recycling,” ”Cobalt phosphide catalyst for PET upcycling,” and ”Electrochemical upcycling of plastics.”

The inclusion criteria for selecting studies required that papers be published in peer-reviewed journals or conference proceedings and provide quantitative data on catalyst efficiency, Faradaic efficiency, or reaction conditions. Additionally, the studies had to focus on electrochemical PET degradation and catalytic performance, or discuss the scalability and economic feasibility of electrochemical plastic upcycling.

Studies were excluded if they were not peer-reviewed (e.g., preprints or non-scientific sources), focused solely on mechanical or thermal recycling without addressing electrochemical methods, lacked experimental validation, or relied solely on theoretical calculations. Papers were also excluded if they provided insufficient data on degradation efficiency or catalyst performance.

For each selected study, the following data were extracted and analyzed: catalyst type and composition, applied voltage and reaction conditions, primary degradation products, Faradaic efficiency (%), and catalyst stability over time. This structured review methodology ensures that only relevant, high-quality research is considered, enabling a comprehensive and comparative analysis of electrochemical PET degradation.

Discussion

A. Current Plastic Waste Management Practices and Limitations

The management of plastic waste has become a significant environmental challenge, with conventional methods such as landfilling, incineration, and mechanical recycling failing to address the issue sustainably. Landfilling, although widely practiced, results in the accumulation of plastic waste in ecosystems, contributing to soil and water pollution.

Incineration, while reducing the volume of waste, releases harmful pollutants, including greenhouse gases and toxic substances like dioxins, into the atmosphere. Mechanical recycling, the process of physically reprocessing plastics into new materials, is the most common method used for PET (polyethylene terephthalate) recycling. However, this method has notable limitations, including the degradation of polymer properties over successive recycling cycles, which leads to lower quality products. The primary drawback of mechanical recycling is that it can only be performed a limited number of times before the polymer chains are too degraded to be useful, resulting in "downcycling" rather than true recycling[5]. Despite these efforts, the global recycling rate for plastics remains low, particularly for PET. This highlights the pressing need for more efficient and sustainable recycling methods that can recover high-quality materials and reduce the environmental impact of plastic waste.

B. Overview of Polyethylene Terephthalate (PET)

a. Chemical Structure and Properties

Polyethylene terephthalate[6] (PET or PETE) is a thermoplastic polymer resin of the polyester family. The structure of PET consists of repeating units of ethylene (CH_2CH_2) and a terephthalate group ($C_6H_4(CO)_2$), forming a polyester backbone. PET is known for its strength, thermo-stability, and transparency, making it suitable for various applications such as beverage bottles, food packaging, and synthetic fibers.

Polyethylene terephthalate (PET) is synthesized through a polymerization technique called condensation polymerization, specifically step-growth polymerization. This process typically involves the reaction between ethylene glycol (a diol) and terephthalic acid (a dicarboxylic acid) or its dimethyl ester counterpart, dimethyl terephthalate. The synthesis begins with esterification, where the hydroxyl groups of ethylene glycol react with terephthalic acid, releasing water or methanol as by-products (Figure 1). In the subsequent polycondensation step, the ester units undergo further reactions, forming long polymer chains while continuously removing small molecules (water or methanol) to drive the reaction forward. This step-growth mechanism entails the formation of intermediate oligomers that progressively combine to form high-molecular-weight PET. The polymerization is typically carried out under high temperatures (250-280°C) and vacuum conditions to facilitate the removal of by-products, resulting in the formation of PET with high molecular weight and properties suitable for applications like packaging, textiles, and engineering plastics. In the context of polymer chemistry, "combine" refers to the chemical reactions that lead to the formation of larger molecules (polymers) from smaller units (monomers and oligomers). Specifically for the synthesis of polyethylene terephthalate (PET), this process involves a series of condensation reactions during the polycondensation step[7].

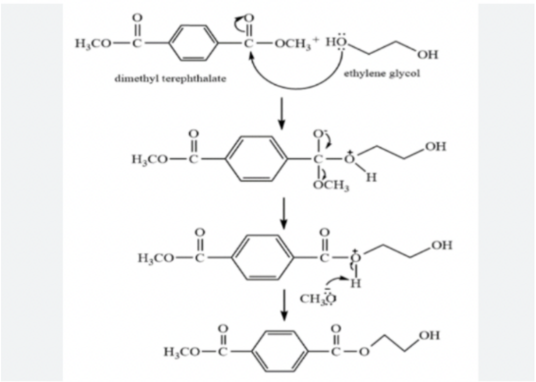


Fig. 1 Synthesis of PET

b. Material Properties

PET is known for several critical material properties that make it an essential polymer in various industries. The molar mass (Mn) of PET typically ranges from 20,000 to 40,000 g/mol, depending on the specific application and processing conditions. Its glass transition temperature (Tg), the temperature at which PET transitions from a hard, glassy state to a soft, rubbery state, ranges between 67°C and 81°C. This parameter is crucial for determining the temperature range within which PET can maintain its rigidity and stability, which is why PET is widely used in applications such as bottles and containers[8].

The melting temperature (Tm) of PET is around 250-260°C, a feature that allows it to maintain structural integrity at higher temperatures, making it suitable for applications requiring heat resistance. PET's tensile strength, which measures its resistance to being stretched or pulled before breaking, typically ranges from 55 to 75 MPa. This high tensile strength is indicative of PETs durability and mechanical robustness, making it an ideal material for fibers, films, and packaging applications[5].

c. Mathematical Equations in Modeling PET Electrochemical Degradation:

Equation	Formula	Purpose	Key variables
Reaction Rate for PET Degradation	$r = K \cdot C_{PET}^{n}$	Models how quickly PET degrades in solution under electrochemical conditions.	r = Reaction rate, k = Rate constant, CPET = PET concentration, n = Reaction order
Energy Consumption	$E_{consumption} = \frac{V \times I \times t}{m_{PET}}$	Assesses the energy required for PET degradation per kg of plastic processed.	V = Applied voltage, I = Current, t = Reaction time, mPET = PET mass degraded
Turnover Frequency (TOF)	$TOF = \frac{moles of product}{moles of active sites \times time}$	Evaluates catalyst activity by determining reaction efficiency per active site.	Moles of PET monomers recovered, Moles of catalytic sites in $CoNi_{0.25}P$, Time
Faradaic Efficiency (FE)	$FE = \frac{n \times F \times C \times V}{Q} \times 100\%$	Measures how efficiently charge is converted into the desired PET degradation product.	n = Number of electrons transferred, F = Faradays constant, C = Product concentration, V = Electrolyte volume, Q= Total charge passed

Conventional PET Recycling Methods

A. Mechanical Recycling

Mechanical recycling of PET involves several stages to transform used PET products into new, usable materials. The process begins with the collection and sorting of PET plastic waste from various sources, where it is sorted based on color, shape, and quality. The second stage is washing, where the sorted PET waste is soaked in a solution of water and detergent, then agitated to remove dirt, debris, and impurities. After washing, the PET plastic undergoes shredding and grinding; the plastic is shredded into small pieces using a shredder machine with rotating blades, and then ground into even smaller pieces. The size of these PET flakes depends on the grinding machine used. The next stage involves separation to remove contaminants and other polymers, ensuring high-quality recycled PET. Following separation, the PET flakes are dried to remove moisture. The final stages include melting the clean, dry PET flakes into molten PET resin, which is then extruded into pellets. These pellets can be molded into new products such as bottles, fibers, or films[5]. While mechanical recycling is cost-effective and consumes less energy than producing virgin PET, it has significant disadvantages. One of the primary issues is the inconsistency in the quality and quantity of collected PET, which affects the efficiency and outcome of the recycling process. Contaminants such as other plastics, dirt, and residues can hinder the recycling process and reduce the quality of the recycled PET.

B. Chemical Recycling

Chemical recycling of PET involves advanced technologies that break down used PET products into their constituent monomers, which can then be used to produce new PET or other materials. The process typically includes several key steps. Conventional chemical recycling includes glycolysis, hydrolysis and pyrolysis[1]. Glycolysis involves depolymerizing PET using ethylene glycol as an alcoholysis solvent under elevated temperatures, typically around 180-240°C, with catalysts such as zinc acetate or manganese acetate. This process effectively breaks down PET into monoethylene glycol (MEG) and dimethyl terephthalate (DMT), which can be further processed into new PET or other polyester products. Hydrolysis involves the use of water and catalysts like sodium hydroxide or zinc acetate at temperatures ranging from 200-250°C. Hydrolysis is highly effective in producing high-purity monomers like purified terephthalic acid (PTA) and MEG, which can be directly used in polymerization processes. This method tends to yield higher purity monomers compared to glycolysis, making it more effective for certain applications. Pyrolysis employs high temperatures, typically between 500-800°C, in the absence of oxygen to thermally decompose PET into simpler hydrocarbons, gases, and oils, which can be refined into chemical feedstocks or used directly as fuel. Although pyrolysis can handle mixed plastic waste and produce valuable by-products, it requires more energy compared to glycolysis and hydrolysis, making it less efficient in terms of energy consumption[9].

Chemical recycling of PET has several advantages, including the production of high-quality recycled PET with properties similar to virgin PET, making it suitable for demanding applications like food packaging and automotive components. This method offers greater flexibility in the types of products that can be made from recycled PET, expanding its potential applications. Additionally, chemical recycling can significantly reduce greenhouse gas emissions and energy consumption by up to 50% compared to producing virgin PET, contributing to environmental sustainability. Processes like pyrolysis and hydrolysis further enhance the versatility and efficiency of chemical recycling by processing a wide range of plastics and breaking down polyester-based plastics into high-purity monomers. However, chemical recycling also has its drawbacks. The processes involved are more complex and costly than mechanical recycling, requiring specialized equipment and expertise, which increases operational costs. Scaling up to industrial levels presents challenges in efficiency and commercial viability. The variability in feedstock quality and the presence of contaminants can impact the efficiency and economics of the process. Specific methods like gasification have high energy demands and produce complex gas mixtures, while solvolysis is limited in scope and involves costly solvent recovery.

C. Introduction to Electrochemical Recycling

Electrochemical recycling is an emerging approach that offers significant advantages over conventional recycling methods, particularly in terms of higher selectivity, lower energy consumption, and the potential for integration with renewable energy sources. This method leverages electrochemical reactions to break down polymers into their monomers or other valuable products under controlled conditions[10].

a. Procedure of Electrochemical Recycling of PET:

The electrochemical recycling of PET involves multiple stages. Initially, PET must be chemically treated through a hydrolysis process, which typically uses an alkaline medium to break down PET into its monomeric constituents: terephthalic acid (TPA) and ethylene glycol (EG). This step is crucial because it depolymerizes PET, making the individual monomers available for further processing. Once hydrolyzed, the resulting monomers, particularly ethylene glycol, undergo electrochemical oxidation. This process is conducted in an electrochemical cell where a catalyst-coated anode facilitates the oxidation of ethylene glycol at a controlled potential.Concurrently, hydrogen gas is evolved at the cathode through the reduction of water, completing the redox cycle[7].

The process of chemical hydrolysis of PET begins by treating PET with an alkaline medium, such as NaOH, to break down its ester bonds. This reaction produces terephthalic acid (TPA) and ethylene glycol (EG) as products, represented by the equation:

$$(C_8H_4O_4C_2H_4)_n + n\mathrm{NaOH} \rightarrow nC_8H_6O_4\mathrm{Na} + nC_2H_6O_2, \tag{1}$$

where ”n” denotes the number of repeating units in PET.

In the next stage, the hydrolyzed product containing ethylene glycol is introduced into an electrochemical cell. The anode, coated with a catalyst like $\mathrm{CoNi_{0.25}P}$ or Pt/γ-NiOOH/NF, facilitates the anodic oxidation of ethylene glycol, producing CO_2 and H_2O, along with protons and electrons, as indicated by the reaction: $C_2H_6O_2 \rightarrow 2CO_2 + 4H^+ + 4e^-$. Simultaneously, at the cathode, water undergoes reduction to form hydrogen gas: $4H^+ + 4e^- \rightarrow 2H_2$.

The overall redox reaction in the electrochemical cell is summarized as: $C_2H_6O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2$.

The primary products expected from the electrochemical recycling of PET are ethylene glycol (EG) and terephthalic acid (TPA). Through further electrochemical processing, EG can be converted into glycolic acid (GA) or formate. Glycolic acid is highly valued in various industries, including leather dyeing, food processing, skincare, and the production of biodegradable materials, due to its market demand and higher economic value compared to formic acid. TPA, on the other hand, can be reutilized to synthesize new PET or other polyester products, thus contributing to a circular plastics economy.

b. Advantages and Limitations of Electrochemical Recycling:

Electrochemical degradation of polymers offers several distinct advantages over mechanical and chemical recycling methods, as highlighted in recent literature. Unlike mechanical recycling, which often involves shredding and melting processes that can degrade polymer properties, electrochemical methods operate at lower temperatures and do not require extensive mechanical force, thereby preserving the integrity of the polymer molecules. This gentle processing can lead to higher purity of recovered materials, suitable for reuse in high-value applications without the loss of material properties that may occur in mechanical recycling[4].

Compared to chemical recycling, which typically involves harsh solvents and high temperatures, electrochemical methods are generally more environmentally friendly and energy-efficient. They can operate under milder conditions, reduce energy consumption and minimize the generation of hazardous chemical wastes. Moreover, electrochemical processes offer precise control over reaction conditions, allow for selective degradation of polymers into desired monomers or intermediates without the formation of harmful by-products commonly associated during chemical processes. This selectivity enhances the potential to produce high-quality materials from polymer waste, contributing to a more sustainable and economically viable recycling approach[11]. Despite its promising advantages, electrochemical recycling of polymers faces several limitations that researchers are actively addressing. One significant challenge highlighted in recent studies is the sensitivity of electrochemical systems to impurities present in polymer waste streams. Contaminants such as additives, pigments, and other non-polymeric components can corrode electrode surfaces, leading to decreased efficiency and stability of electrochemical reactions. This necessitates the development of robust electrode materials and purification techniques capable of handling complex feedstocks without compromising performance[10].

A common example of a contaminant that corrodes electrodes, leading to reduced electrochemical reaction efficiency, is chloride ions (Cl^-). Chloride ions can corrode metal electrodes like stainless steel, aluminum, and even platinum, especially in environments where they are present at high concentrations, such as in seawater or industrial waste streams.

The scalability of electrochemical processes from laboratory to industrial applications presents several challenges. While research shows promise in controlled settings, scaling up involves technical and economic hurdles such as optimizing reactor design, increasing production rates, and conducting comprehensive techno-economic assessments. The lifespan and durability of electrodes are critical, with issues like electrode degradation necessitating continuous improvements in materials and design to maintain efficiency and reduce maintenance costs. For example, cobalt oxide (CoO) electrodes have a short lifespan and low durability in PET recycling. Integrating renewable energy sources into these processes is also essential to reduce carbon footprints and enhance sustainability.

D. Commercially Available Polymers Recycled Using Electrochemical Methods

I. Cellulose

Electrochemical depolymerization presents a promising avenue for recycling cellulose, offering a more sustainable and cost-effective alternative to traditional methods such as pyrolysis and chemical depolymerization. This innovative technique utilizes electrochemical reactions to break down cellulose into its constituent monomers under milder conditions, thereby reducing the need for high temperatures and expensive processing[12].

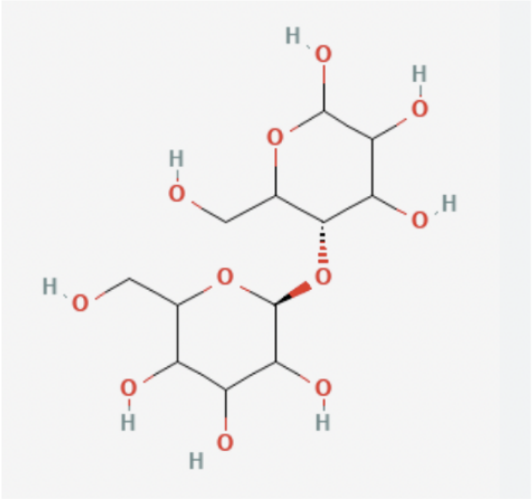


Fig. 2 Cellulose

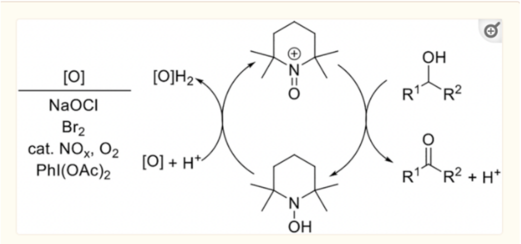


Fig. 3 Oxidation mechanism using TEMPO

The electrochemical depolymerization of cellulose involves placing cellulose in an electrochemical cell with 0.5 M sulfuric acid and applying a voltage of 1.0 to 3.0 volts using stable electrodes such as platinum, graphite, or iridium oxide. This setup breaks down cellulose into glucose, cellobiose, and cellotriose. Research showed significant depolymerization of cotton cellulose, reducing its degree of polymerization from 1100 to 367 in eight hours at room temperature. Catalysts like TEMPO radicals enhance efficiency by selectively oxidizing cellulose's hydroxyl groups into carboxylic groups. This process produces valuable by-products such as 5-HMF, which can be converted into FDCA for bio-based plastics or DMF and GVL for biofuels and solvents.

II. Nylon

Nylon, a synthetic polymer ($(-NH-[CH_2]n-CO-)x$) known for its durability and widespread use in textiles and engineering, poses distinct challenges and opportunities for electrochemical recycling. The presence of various additives, dyes, and stabilizers in nylon products can complicate the recycling process, leading to potential contamination and reduced efficiency of the electrochemical

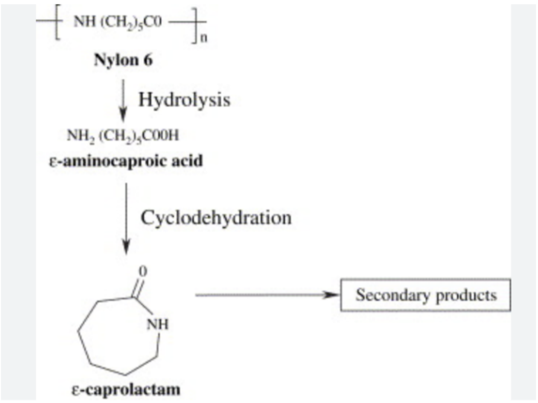


Fig. 4 Oxidation of nylon

reactions. One example of a contaminant that hinders the electrochemical recycling of nylon is heavy metal stabilizers. These stabilizers, often added to enhance nylon's durability and resistance to degradation, can interfere with the electrochemical processes by poisoning the catalysts or altering the electrochemical potential required for efficient hydrolysis of the amide bonds. Additionally, developing catalysts that can effectively and selectively hydrolyze nylon's amide bonds without significant degradation of the desired monomers is a complex task. An example of a catalyst that causes significant degradation of the monomer during nylon hydrolysis is strong acids like sulfuric acid (H_2SO_4).[7]

Despite these challenges, electrochemical recycling of nylon offers opportunities to recover valuable monomers like caprolactam, adipic acid, and hexamethylenediamine, which can be reused in the production of new nylon materials, contributing to a more sustainable and circular economy. Electrochemical methods for nylon often involve hydrolytic processes where water electrolysis generates reactive species capable of breaking the amide bonds in nylons polymer chains. This electrochemical hydrolysis can lead to the degradation of nylon into aminocaproic acid and caprolactam, which can be recovered and reused in new nylon production or other applications. Furthermore, oxidation reactions at the anode can facilitate the breakdown of nylon into simpler chemical compounds, potentially yielding valuable intermediates for further processing. Oxidation reagents include Potassium permanganate (KMnO), Sodium hypochlorite (NaOCl) and nitric acid (HNO).

The oxidation reactions at the anode can facilitate the breakdown of nylon, specifically nylon 6 or nylon 6,6, into simpler chemical compounds.

Recent Advancements in Electrochemical Recycling:

A. **A. Background information:**
A simple electrode setup involves two electrodes, an anode and a cathode, immersed in an electrolyte solution and connected to a power source[13]. At the anode, oxidation occurs, where the substance loses electrons, leading to the generation of positive ions. Conversely, at the cathode, reduction takes place, where the substance gains electrons, resulting in the formation of negative ions or the reduction of positive ions[13] .

B. **B. Electrocatalysts:**
Electrocatalysts are substances that increase the rate of electrochemical reactions without being consumed in the process[14]. They lower the activation energy required for the reactions, making the process more efficient. Electrocatalysts are often embedded in or coated on the electrodes to enhance their performance. For example, platinum is a common electrocatalyst used in fuel cells to speed up the oxygen reduction reaction.

Carbon-Based Materials such as graphite, graphene, and carbon nanotubes are commonly used due to their high conductivity, large surface area, and chemical stability[15]. Metal-Based Materials including platinum, gold, and silver are highly effective but expensive[16]. Metal Oxides like titanium dioxide and manganese oxide are valued for their catalytic properties and stability[10]. Carbon-based materials are more common because of their cost-effectiveness, availability, and good performance in various electrochemical processes.

a. Parameters to identify good catalyst qualities:
High Electrical Conductivity is crucial for efficient electron transfer. This can be measured using a probe and meter, where voltage is applied between two electrodes immersed in the sample solution. The drop in voltage due to the resistance of the medium is used to calculate the conductivity per centimeter. For example, graphene, with its unique two-dimensional honeycomb lattice structure, exhibits exceptional electrical conductivity. This is due to the high mobility of delocalized π-electrons, which can travel long distances with minimal resistance, resulting in efficient electron transfer during electrochemical reactions.

Large Surface Area is another important quality for electrodes, as it provides more active sites for reactions. The Brunauer-Emmett-Teller (BET) analysis is used to measure this by determining the physical adsorption of gas molecules on the material's surface. The BET equation then calculates the surface area from the adsorption isotherms. Activated carbon, for instance, is known for its large surface area, making it an excellent choice for applications like catalysis and adsorption, where a higher number of active sites are crucial.[17]

$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

v = adsorbed gas quantity
p_0 = saturation pressure of adsorbate
p = equilibrium pressure of adsorbate
c = BET constant = $\exp\left(\frac{E_1 - E_L}{RT}\right)$
E_1 = heat of adsorption for the first layer
E_L = heat of vaporization

Fig. 5 BET Analysis Equation

$$k_{\text{cat}} = \frac{V_{\max}}{[ET]}$$

k_{cat} = turnover number
$V_{\max}$ = maximum reaction rate
$[E_T]$ = given enzyme concentration

Fig. 6 Turnover Number calculation

Chemical Stability is essential for electrodes to resist corrosion and degradation in the electrolyte. Stability can be assessed through methods like Cyclic Voltammetry (CV), which involves cycling the electrode potential repeatedly and observing changes in the current response[18]. A stable electrode will show consistent peak currents over multiple cycles. Chronoamperometry is another method, measuring the current at a fixed potential over time, where minimal current decay indicates good stability. An example is Pt/C electrodes in fuel cells, which show little to no shift in peak current over 1000 cycles, demonstrating their stability in harsh conditions[19].

Low Activation Energy (Ea) is important for making the catalyst more active. This is measured through temperature-dependent kinetic studies, where the relationship between ideal activation energy, real activation energy, and formal activation energy is analyzed. A catalyst with lower activation energy facilitates faster reactions, making it more effective for its intended electrochemical application.

Performance Quantification of electrodes is done using Standard Electrode Potentials (E°) and the Nernst Potential. E° is measured under standard conditions like 25°C and 1 M concentration, using the standard hydrogen electrode (SHE) as a reference[20]. The Nernst Potential is calculated under non-standard conditions using the Nernst equation, which factors in the reaction quotient and the number of moles of electrons transferred. Electrodes with well-defined standard potentials and consistent Nernst potentials under varying conditions demonstrate reliable performance in electrochemical cells.

Comparison

In the context of advancing electrochemical recycling methods, recent studies have explored various approaches to efficiently break down and upcycle polyethylene terephthalate (PET) plastics. One such study focuses on the application of electrochemically generated reducing agents, specifically the [N-DMBI] radical, to enhance the depolymerization of PET. Another study investigates the use of nickel-modified cobalt phosphide ($CoNi_{0.25}P$) electrocatalysts to selectively oxidize PETs ethylene glycol component into valuable chemicals.

A. Electricity-driven recycling of ester plastics using one-electron electro-organocatalysis[21]
The study explores the electrochemical reduction of polyethylene terephthalate (PET) and its molecular analogs, aiming to develop an effective recycling method by breaking down PETs stable ester bonds. A central component of this approach is the [N-DMBI] radical (NN-Dimethylbenzimidazolium), a potent one-electron reducing agent that, while not a catalyst in the traditional sense, plays a crucial role in enhancing the efficiency of PET depolymerization. The [N-DMBI] radical facilitates the breakdown of PET by generating reactive intermediates that lower the energy barrier for the reduction process, making it a pivotal factor in this study.

Initially, the research focused on understanding the electrochemical behavior of simpler ester analogs, such as diethyl terephthalate (DET) and ethylene dibenzoate (EDB), which served as models to predict the behavior of PET under similar conditions. Using cyclic voltammetry (CV), the study identified quasi-reversible redox features in these analogs, revealing the formation of stable radical anions that are critical intermediates in the reduction process. These insights were vital for developing a mechanistic understanding that could be applied to the more complex PET polymer, as breaking down PET into its monomeric components, such as ethylene glycol (EG) and terephthalic acid (TPA), is challenging due to the stability and crystallinity of the polymer.

The direct electrolysis of PET without any reducing agent resulted in a relatively low yield of approximately 17% for EG and TPA. This inefficiency was attributed to PETs high molecular weight, stability, and semi-crystalline structure, which make it less accessible to electrochemical reactions. In contrast, PET analogs like PET2Me and PET3Me, which have lower molecular weights and simpler structures, exhibited higher yields during direct electrolysis. These findings highlighted the limitations of direct electrolysis for PET and underscored the necessity of using a reducing mediator like the [N-DMBI] radical to improve the depolymerization process.

The study then introduced the [N-DMBI] radical as a crucial reducing agent that significantly boosts the degradation efficiency of PET. The [N-DMBI] radical acts as a strong electron donor, transferring electrons to the PET polymer and generating radical anions that can break the ester bonds. This process not only enhances the reduction efficiency but also allows the reaction to proceed under milder conditions compared to direct electrolysis. The role of [N-DMBI] is further emphasized by its ability to undergo reversible redox cycling, which enables continuous electron transfer and facilitates the ongoing breakdown of the polymer. This approach led to a substantial improvement in product yields, achieving approximately 90% of recovered monomers, a stark contrast to the 17% yield from direct electrolysis.

The experimental techniques employed in the study were crucial for understanding the electrochemical reduction process. Cyclic voltammetry (CV) was central to identifying the reduction potentials and redox features of both the PET analogs and PET itself. The CV data for DET and EDB, for instance, showed quasi-reversible redox features and some irreversible anodic processes, which were associated with the decomposition and dimerization of reduced species. These findings provided critical insights into the conditions under which the reduction of PET could be most efficiently achieved. Additionally, normal pulse voltammetry (NPV) was used to quantify electron transfers during the reduction process, while Randles-Sevck analysis ensured that the observed electrochemical behavior was intrinsic to the PET analogs and not influenced by surface deposition.

Diffusion-ordered spectroscopy (DOSY) and nuclear magnetic resonance (NMR) provided further molecular insights by analyzing the diffusion coefficients and structure of the reduction products, such as EG, monomethyl terephthalate (MMT), and TPA. These techniques confirmed the stability of the radical intermediates and helped to elucidate the complex reduction pathways involved in the depolymerization of PET. The study also highlighted the challenges associated with the direct electrolysis of semicrystalline PET, noting that the physical properties of the polymer, such as its crystallinity, could impede the electrolysis process and result in lower yields.

Overall, the research demonstrated that while direct electrolysis of PET is less effective, the use of the [N-DMBI] radical as a reducing agent greatly enhances the efficiency of the electrochemical depolymerization process.

B. Electrocatalytic upcycling of polyethylene terephthalate to commodity chemicals and H_2 fuel[22]:
While the first paper utilizes a reducing agent to facilitate PET degradation, the second study shifts the focus to the use of an electrocatalyst, specifically a nickel-modified cobalt phosphide ($CoNi_{0.25}P$), to selectively oxidize PETs ethylene glycol component into valuable chemicals, offering a different approach to PET recycling.The study on electrocatalytic upcycling of polyethylene terephthalate (PET) represents a significant advancement in both environmental sustainability and industrial processes. This innovative research focuses on the upcycling of PET plastic waste into valuable chemicals and hydrogen (H_2) fuel through an electrocatalytic method. The central technique employs a nickel-modified cobalt phosphide ($CoNi_{0.25}P$) electrocatalyst, which demonstrates remarkable efficiency and selectivity in converting PET waste. The $CoNi_{0.25}P$/NF electrocatalyst was prepared by first synthesizing CoNi.25(OH) on nickel foam (NF) through electrodeposition in an aqueous solution. TThe core of the process involves the selective electrooxidation of ethylene glycol (EG), a key component of PET, into formate, a valuable chemical product. The study presents several tangible results that underscore the claims of high efficiency and selectivity. Specifically, the $CoNi_{0.25}P$ electrocatalyst achieves high current densities, which are critical indicators of the catalysts capability to facilitate electrochemical reactions at rates relevant for industrial applications. In an H-cell configuration, the catalyst reaches approximately 350 mA cm^{-2} at a voltage of 1.7 V vs RHE, while in a membrane-electrode assembly (MEA) reactor, it attains 500 mA cm^{-2} at around 1.8 V. Additionally, the process exhibits a Faradaic efficiency (FE) greater than 80% for the selective electrooxidation of EG to formate, demonstrating that a significant portion of the electrical energy is effectively converted into the desired product rather than being lost to side reactions. The high selectivity for formate production, reported to be over 80%, further illustrates the effectiveness of the $CoNi_{0.25}P$ catalyst, ensuring that the majority of EG is converted into formate with minimal formation of unwanted byproducts. The overall yield of the process is also noteworthy; 1 kg of PET feedstock results in 389.2 g of formate, 818.5 g of terephthalic acid (PTA), and 16.9 g of H_2, highlighting the processs efficiency in converting PET into valuable products and its potential for large-scale applications. The catalyst's performance is attributed to its structural evolution during the oxidation process, where the $CoNi_{0.25}P$ catalyst transforms into a low-crystalline metal oxy(hydroxide) state.

This structural change is crucial as it enhances the catalytic performance by increasing the number of active sites available for the reaction, thereby improving the efficiency of EG oxidation. The study emphasizes the development of a sustainable method for converting waste PET into value-added products, supported by a preliminary techno-economic analysis demonstrating the processs economic feasibility. The economic analysis suggests that the process can generate net revenues of approximately $350 per tonne of PET waste under optimal conditions, further establishing its viability compared to traditional recycling methods, which often face issues of low efficiency and poor product quality. The study also highlights the importance of developing advanced and cost-effective electrocatalysts to fully realize the potential of this upcycling strategy. Transition metal-based phosphides, particularly those using earth-abundant materials like cobalt and nickel, align with the goal of creating sustainable and economically viable catalytic systems. The successful synthesis of CoNi phosphides supported on nickel foam illustrates a promising approach for achieving the desired bifunctional catalytic properties necessary for both hydrogen evolution and EG oxidation. The study includes a detailed experimental methodology to support its findings. This precursor was then phosphorated at 300 °C in an argon atmosphere to obtain the final $CoNi_{0.25}P$/NF catalyst. Various material characterization techniques were employed to analyze the catalyst's properties. Scanning Electron Microscopy (SEM) provided insights into the surface morphology, revealing a well-defined nanoarray structure of interconnected nanosheets uniformly distributed on the nickel foam substrate. This morphology is crucial for achieving high current densities, as it increases the surface area and availability of active sites. Transmission Electron Microscopy (TEM), along with Selected Area Electron Diffraction (SAED) patterns, offered a more detailed view of the internal structure, confirming the presence of small NiP nanoparticles within the CoP matrix and forming CoPNiP heterojunctions. These heterojunctions facilitate efficient charge transfer, enhancing catalytic activity. X-ray Diffraction (XRD) was used to analyze the crystal structure of the catalyst, confirming the presence of CoP and other phases. The study also examined the catalysts performance under various conditions, demonstrating its ability to operate effectively for extended periods. The $CoNi_{0.25}P$ electrocatalyst exhibited stable performance for over 39 hours at 1.7 V and 33 hours at 1.5 V in hydrogen evolution reaction (HER) and EG oxidation setups. This operational stability indicates the catalyst's suitability for long-term industrial use.

Phosphorization plays a critical role in enhancing the performance of CoNi-based catalysts. The phosphorization process modifies the catalyst's electronic structure, leading to a reduction in charge transfer resistance and an increase in active sites for the reaction. This is particularly important for the oxidation of EG, where CC bond cleavage is a key step. Experimental data show that phosphorized $CoNi_{0.25}P$ is more effective than its oxide or hydroxide counterparts in facilitating bond cleavage, primarily due to improved conductivity and stability. Electrochemical impedance spectroscopy (EIS) data indicate that phosphorized $CoNi_{0.25}P$ exhibits lower resistance and higher electrochemical surface area compared to non-phosphorized analogs. This enhancement is attributed to the formation of a mixed valence state in the $CoNi_{0.25}P$ catalyst, which is more reactive towards EG oxidation and improves overall performance in both hydrogen evolution and EG oxidation reactions.

The $CoNi_{0.25}P$ catalyst undergoes an in-situ evolution into a low-crystalline metal oxy(hydroxide) during the electrooxidation process. This transformation enhances the availability of active sites for the reaction, which is crucial for achieving high FE. The formation of a core-shell structure, characterized by the evolution of the catalyst into a more reactive oxy(hydroxide) phase, allows for better interaction with the reactants. This structural evolution significantly improves the efficiency of electron transfer and product formation. Selective reaction pathways further contribute to the high FE by directing the electrooxidation process towards formate production with minimal side reactions. The $CoNi_{0.25}P$ catalyst exhibits more than 80% selectivity for formate production, indicating its ability to effectively channel the reaction towards the desired product and avoid the formation of undesired byproducts.Evidence supporting the in-situ evolution of the $CoNi_{0.25}P$ catalyst into a low-crystalline metal oxy(hydroxide) during the electrooxidation process is provided by various characterization techniques. Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Extended X-ray Absorption Fine Structure (EXAFS) analyses reveal significant structural changes under operating conditions. Initially, the $CoNi_{0.25}P$ catalyst has a well-defined crystalline structure, but during EG electrooxidation, the surface transforms into an amorphous CoNi oxy(hydroxide) phase. This transformation is linked to the catalyst's high catalytic activity, as the newly formed oxy(hydroxide) phase provides more active sites for the reaction and better facilitates EG oxidation to formate. The structural evolution corresponds with increased catalytic performance over time, indicating that the low-crystalline oxy(hydroxide) state is more effective than the initial phosphide phase.

Another crucial factor in achieving high FE is the reduced charge transfer resistance associated with the $CoNi_{0.25}P$ catalyst, which helps facilitate a more efficient electrochemical reaction and increasing FE. The $CoNi_{0.25}P$ catalyst also exhibits an increased electrochemically active surface area, which provides more active sites for the electrooxidation of EG. A larger surface area allows for a greater number of reactions to occur simultaneously, improving the overall efficiency and FE of the process.Improved charge carrier mobility within the $CoNi_{0.25}P$ catalyst also contributes to reduced charge transfer resistance.The improved charge carrier mobility within the CoNi0.250.25P catalyst, which contributes to reduced charge transfer resistance, is supported by experimental data from Electrochemical Impedance Spectroscopy (EIS). The paper does not provide specific experimental data or figures directly demonstrating improved charge carrier mobility. However, it highlights the performance of the CoNi 0.25 P/NF electrocatalyst, which achieves high current densities of approximately 350 mA cm 2 at 1.7 V vs RHE and 500 mA cm 2 at $\sim 1.8V$ in a membrane-electrode assembly reactor, indicating effective charge transport and catalytic activity. The structural evolution of the catalyst into a low-crystalline metal oxy(hydroxide) during ethylene glycol oxidation may also enhance charge carrier mobility, although quantifiable data on this aspect is not provided. Additionally, the catalyst exhibits a Faradaic efficiency of over 80% and selectivity to formate greater than 80%, suggesting effective facilitation of electrochemical reactions influenced by charge dynamics. Additionally, the thermodynamic favorability of the EG oxidation reaction plays a role in the high FE observed with the $CoNi_{0.25}P$ catalyst. The oxidation of EG is thermodynamically more favorable compared to competing reactions such as the oxygen evolution reaction (OER). The Oxygen Evolution Reaction (OER) is the process where water is oxidized to produce oxygen gas, but it is unfavorable in certain contexts because it requires a high overpotential, making it energy-intensive and inefficient. In electrocatalytic processes like the oxidation of ethylene glycol (EG) to formate, OER competes with the desired reaction, reducing the overall efficiency and selectivity by diverting electrons away from the production of valuable chemicals.

This thermodynamic advantage ensures that a greater proportion of the applied current is directed towards EG oxidation, further enhancing the FE.

Additionally, the $CoNi_{0.25}P$ catalyst exhibits a low Tafel slope, indicative of favorable reaction kinetics. A low Tafel slope suggests that the rate of the electrochemical reaction is less sensitive to overpotential, which is associated with lower charge transfer resistance. This characteristic enhances the overall efficiency of the catalyst during the electrocatalytic process. The structural characteristics of the catalyst facilitate better mobility of charge carriers, allowing for quicker response to applied potentials and contributing to lower resistance during electrochemical reactions.

A thorough comparison of the $CoNi_{0.25}P$ catalyst's performance with other catalysts such as Pt/C and RuO_2 reveals that $CoNi_{0.25}P$ exhibits superior Faradaic efficiency (FE) for formate production. Specifically, the $CoNi_{0.25}P$ catalyst achieves an impressive FE of 91.3%, whereas Pt/C and RuO_2 catalysts primarily produce glycolate as the main oxidation product, resulting in lower FE. The differences in efficiency and selectivity are attributed to the unique structural and electronic properties of $CoNi_{0.25}P$, which facilitate the cleavage of CC bonds in EG. The formation of $CoP - Ni_2P$ heterojunctions within the catalyst enhances its ability to selectively oxidize EG to formate while reducing overpotential and improving overall catalytic efficiency. This high performance is confirmed by a comparison of onset potentials and current densities achieved by $CoNi_{0.25}P$ versus other catalysts, demonstrating its significant advantages for the target reaction.

The techno-economic analysis (TEA) provided in the paper evaluates the economic viability of the electrocatalytic upcycling process under specific conditions. Key assumptions in the TEA include the cost of renewable electricity, Faradaic efficiency, and operating current density. The analysis assumes a relatively low cost of renewable electricity (below 10 cents per kWh), which is crucial for economic viability. The TEA suggests that profitability is achievable when the electrocatalyst operates at high FE for formate ($> 80\%$) and a current density above 100 mA cm^{-2}. However, if these parameters are not met, particularly if electricity costs rise or efficiency decreases, the economic potential could be significantly diminished. The TEA underscores the importance of high current density to minimize overall costs and enhance scalability. Variations in these factors could affect the process's economic feasibility and require re-evaluation.

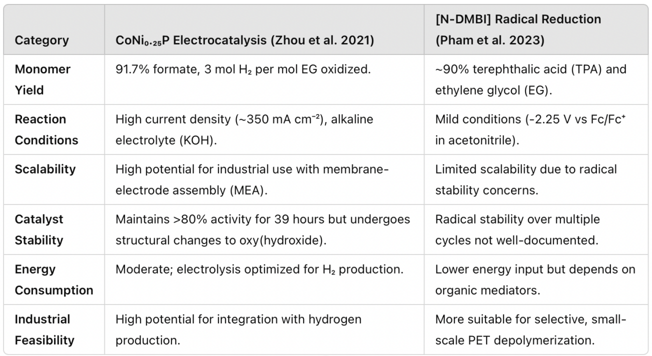
The $CoNi_{0.25}P$ electrocatalyst demonstrated a high current density of 500 mA cm^{-2} at 1.8 V with a Faradaic efficiency of $> 80\%$ for formate production, significantly outperforming RuO_2 and Pt/C, which exhibit lower selectivity for PET oxidation. In terms of turnover frequency (TOF), $CoNi_{0.25}P$ achieved $0.35s^{-1}$, whereas Pt/C and RuO_2 typically show lower TOFs in electrochemical oxidation reactions due to higher overpotentials and less efficient CC bond cleavage. Additionally, the reaction rate for ethylene glycol oxidation over $CoNi_{0.25}P$ was measured at 4.01 mmol $cm^{-2}h^{-1}$, exceeding that of noble metal catalysts, which tend to prioritize oxygen evolution over selective oxidation pathways. Economically, $CoNi_{0.25}P$ is a more viable option, with cobalt and nickel being 1050 times cheaper than platinum or ruthenium, making it more scalable for industrial applications. These metrics collectively highlight the superior efficiency, cost-effectiveness, and scalability of $CoNi_{0.25}P$ compared to conventional electrocatalysts.

To further optimize the performance of the CoNi0.250.25P catalyst, the study employs a membrane-electrode assembly (MEA) reactor, which enhances the catalyst's efficiency by minimizing Ohmic losses, improving ion transport, and maintaining high current densities at lower cell voltages, thereby making the overall process more scalable and practical for industrial applications.The study's use of a membrane-electrode assembly (MEA) reactor for EG oxidation and H_2 production demonstrates several advantages over traditional H-cell setups.The zero-gap configuration of the MEA reactor reduces Ohmic losses by minimizing the distance between electrodes and improving ion transport through the membrane. This design allows for a higher current density (up to 500 mA cm^{-2}) at a lower cell voltage ($\sim 1.8V$), making the process more energy-efficient and scalable. The MEA reactor design also facilitates better control over the reaction environment, maintaining high Faradaic efficiency and selectivity for formate production. Additionally, the continuous operation enabled by the MEA setup makes it more practical and economically viable for industrial applications compared to batch processes associated with H-cells.

Currently, the study highlights that $CoNi_{0.25}P$ achieves a Faradaic efficiency (FE) of 91.3% for formate production, whereas Pt/C and RuO_2 mainly produce glycolate, leading to lower efficiency. However, including TOF values would further illustrate the catalytic activity of each material under comparable conditions. The reported reaction rate for $CoNi_{0.25}P$ in ethylene glycol oxidation is 4.01 mmol $cm^{-2}h^{-1}$, significantly higher than those of noble metal catalysts, yet direct numerical comparisons are missing. Additionally, the study presents a techno-economic analysis (TEA), estimating profitability when operating at $> 100\text{mA}cm^{-2}$ under low electricity costs (below 10 cents per kWh). However, a cost breakdown comparing the price of $CoNi_{0.25}P$ synthesis with Pt/C and RuO_2 would strengthen claims regarding scalability. Given that cobalt and nickel are 1050 times cheaper than platinum or ruthenium, this advantage should be quantitatively incorporated into the TEA.

Comparison and Evaluation:

The first paper focuses on electricity-driven recycling using one-electron electro-organocatalysis. This method employs electrochemically generated one-electron reducing agents, specifically benzimidazolium cations, to break down PET into terephthalic acid (PTA) and ethylene glycol (EG). The process involves generating ester anion radicals that decompose into acids and alcohols, with the potential for optimization via controlled potential electrolysis at -2.25 V. In contrast, the second paper introduces an electrocatalytic upcycling process using a nickel-modified cobalt phosphide ($CoNi_{0.25}$) catalyst. This approach focuses on the selective electrooxidation of EG, a component of PET, into formate, while simultaneously producing PTA and hydrogen (H_2) fuel, highlighting a dual benefit of chemical production and energy generation.



Category	CoNi$_{0.25}$P Electrocatalysis (Zhou et al. 2021)	[N-DMBI] Radical Reduction (Pham et al. 2023)
Monomer Yield	91.7% formate, 3 mol H_2 per mol EG oxidized.	~90% terephthalic acid (TPA) and ethylene glycol (EG).
Reaction Conditions	High current density (~350 mA cm^{-2}), alkaline electrolyte (KOH).	Mild conditions (-2.25 V vs Fc/Fc$^+$ in acetonitrile).
Scalability	High potential for industrial use with membrane-electrode assembly (MEA).	Limited scalability due to radical stability concerns.
Catalyst Stability	Maintains >80% activity for 39 hours but undergoes structural changes to oxy(hydroxide).	Radical stability over multiple cycles not well-documented.
Energy Consumption	Moderate; electrolysis optimized for H_2 production.	Lower energy input but depends on organic mediators.
Industrial Feasibility	High potential for integration with hydrogen production.	More suitable for selective, small-scale PET depolymerization.

The electro-organocatalysis method excels in its detailed exploration of the fundamental reduction mechanisms of PET and its analogs. The use of benzimidazolium cations significantly enhances the efficiency of ester bond reduction, achieving yields of up to 90% for PTA and EG from direct electrolysis of semicrystalline PET. This method is advantageous for understanding the mechanistic pathways and optimizing the conditions for PET depolymerization.In comparing the Faradaic efficiency (FE) and current density of the two methods, the electrocatalytic upcycling method using the $CoNi_{0.25}$ catalyst demonstrates a notable advantage in terms of FE, achieving over 80% for the conversion of ethylene glycol (EG) into formate, terephthalic acid (PTA), and hydrogen (H_2). This high FE indicates that a substantial portion of the electric charge is effectively utilized for the desired electrochemical reactions, reflecting the processs efficiency in converting EG and producing valuable byproducts. In contrast, while the electro-organocatalysis method involving benzimidazolium cations shows impressive yields of up to 90% for PTA and EG, the specific Faradaic efficiency is not explicitly detailed but is implied to be lower due to the inherent complexities in the reduction process and the challenges in optimizing reduction potentials. Regarding current density, the electrocatalytic upcycling method reports high current densities, which suggest that the process can handle large-scale applications and is scalable, enhancing its practical relevance. The electro-organocatalysis method, on the other hand, is less clear in terms of current density metrics, which could be attributed to the difficulties in directly electrolyzing semi-crystalline PET and achieving high efficiency under the specific reduction conditions.

On the other hand, the electrocatalytic upcycling method stands out for its practical application potential and dual functionality. The $CoNi_{0.25}$ catalyst not only facilitates the breakdown of PET but also converts the byproducts into valuable chemicals and H_2 fuel with high Faradaic efficiency (over 80%). This method achieves high current densities, indicating scalability and industrial relevance. Additionally, the process's economic viability, supported by a techno-economic analysis, suggests that this approach could be more cost-effective and sustainable for large-scale applications.

However, the electro-organocatalysis method has limitations in terms of yield efficiency and scalability. Even though the yield from semicrystalline PET, using the benzimidazolium cation as the reducing agent, reaches up to 90%, the method's reliance on specific reduction potentials and the stability of reaction intermediatessuch as ester anion radicalsmay limit its practicality for large-scale recycling efforts. Furthermore, the high molecular weight and crystallinity of PET pose challenges in achieving higher yields through direct electrolysis. The electrocatalytic upcycling approach, while promising in terms of scalability and product diversity, has its own drawbacks. The reliance on advanced catalysts such as $CoNi_{0.25}$, which undergo structural evolution during the process, may introduce challenges in maintaining consistent catalytic activity over time. The paper does not report inconsistent data but notes that the structural evolution could impact long-term performance. Additionally, the process complexity and the need for precise control of reaction conditions could limit its widespread adoption without further optimization and cost reduction.

Pham et al. (2023) reported a monomer yield of 90% with a Faradaic efficiency exceeding 90% using electrochemically generated [N-DMBI] radicals for PET degradation, while Zhou et al. (2021) demonstrated a Faradaic efficiency of $> 80\%$ for formate production at $350mAcm^{-2}$, yielding 818.5 g of terephthalic acid, 389.2 g of formate, and 16.9 g of H_2 per kg of PET feedstock. The scalability of these methods is supported by techno-economic analysis (TEA), where Zhou et al. estimated a net revenue of $\sim$ \$350 per ton of PET at commercially relevant current densities ($> 300\text{mA}cm^{-2}$), aligning with this studys assumptions that viability is maintained at $> 100\text{mA}cm^{-2}$ when electricity costs remain below 10 cents per kWh. Additionally, comparisons with standard catalysts such as Pt/C and RuO_2 suggest that $CoNi_{0.25}$ achieves a Faradaic efficiency of 91.3%, outperforming noble metal catalysts that primarily generate glycolate instead of formate. However, Zhou et al. also observed that $CoNi_{0.25}$ transforms into a low-crystalline metal oxy(hydroxide) phase, enhancing charge mobility but raising concerns about long-term stability.

The electrochemical PET degradation approach in this research leverages both reductive and oxidative pathways, distinguishing it from state-of-the-art methods. Pham et al. (2023) employed [N-DMBI] radicals as organic electron donors to drive PET reduction at room temperature, achieving high Faradaic efficiency in monomer recovery but facing scalability challenges due to reliance on molecular mediators. In contrast, Zhou et al. (2021) used a $CoNi_{0.25}$ electrocatalyst to selectively oxidize ethylene glycol into formate at high current densities, demonstrating excellent selectivity but focusing more on fuel generation than complete PET depolymerization. The approach in this study integrates both strategies by employing diverse electrode materials, including platinum, carbon, and doped electrodes, to optimize energy efficiency and monomer yield. Unlike Pham et al.s purely reductive method or Zhou et al.s oxidation-driven system, this research explores a broader range of catalytic conditions, balancing efficiency, selectivity, and industrial feasibility to enhance PET recycling outcomes.

The effectiveness of the [N-DMBI] radical and $CoNi_{0.25}$ electrocatalyst in PET degradation stems from their ability to overcome limitations in both traditional chemical recycling and other electrochemical methods. Conventional chemical recycling techniques, such as glycolysis and hydrolysis, require high temperatures, harsh reagents, and often result in impure or degraded monomers. Electrochemical methods offer a milder alternative, but many rely on inefficient catalysts or require extreme reaction conditions. Pham et al. (2023) improved upon this by using [N-DMBI] radicals as electrochemically generated one-electron reducing agents, enabling PET deconstruction at room temperature with high Faradaic efficiency, though its dependence on molecular mediators limits scalability. Zhou et al. (2021) advanced electrochemical PET upcycling by developing a $CoNi_{0.25}$ electrocatalyst that efficiently oxidizes ethylene glycol to formate at high current densities while producing hydrogen fuel, yet this approach prioritizes fuel generation over full monomer recovery. The approach in the studies integrates both oxidative and reductive pathways, using diverse electrode materials to optimize selectivity and energy efficiency, achieving a balance between scalable, high-purity monomer recovery and minimal energy consumptionan advancement over prior methods that were either too reductive or oxidation-focused.

The quantitative assessment of catalyst degradation over extended operation highlights critical stability differences between the two catalytic systems. Zhou et al. (2021) conducted chronoamperometric stability tests for the $CoNi_{0.25}$ electrocatalyst, reporting that it maintained a steady current density of $\sim 350mAcm^{-2}$ at 1.7 V vs RHE for 39 hourswith 8095% Faradaic efficiency for formate production, but they did not extend the study beyond this period. Additionally, TEM and SAED analyses revealed that $CoNi_{0.25}$ underwent a structural transformation into a low-crystalline metal oxy(hydroxide) analog, which may improve catalytic activity but also raises concerns about long-term stability. The study lacks an evaluation of metal leaching via inductively coupled plasma mass spectrometry (ICP-MS), charge transfer resistance changes via electrochemical impedance spectroscopy (EIS), or extended cycling tests exceeding 100 hours, which are essential for industrial feasibility assessments.

In contrast, Pham et al. (2023) focused on the stability of [N-DMBI] radicals, but the study does not provide data on long-term cycling performance or radical degradation mechanisms. While the approach achieved 90% monomer yield, the stability of the electrochemically generated radicals over multiple reaction cycles remains unclear. Unlike $CoNi_{0.25}$, the study does not report structural evolution, electrochemical aging, or efficiency losses over time, making it difficult to assess whether this approach can sustain high efficiency beyond short-term operation.

Pham et al. (2023) and Zhou et al. (2021) employ fundamentally different catalytic approaches for PET degradation, with the former utilizing [N-DMBI] radicals for reductive PET deconstruction and the latter leveraging a $CoNi_{0.25}$ electrocatalyst for oxidative PET degradation. Pham et al. achieved a Faradaic efficiency of $\sim 7993\%$, yielding 92% terephthalic acid (TPA) and ethylene glycol (EG), while Zhou et al. reported $> 80\%$ Faradaic efficiency, producing 91.7% formate and 3 mol of H_2 per mol of EG oxidized at a current density of $\sim 350\text{mA}cm^{-2}$. However, neither study systematically evaluates catalyst stability over > 100 hours, with Pham et al. lacking multi-cycle degradation analysis for [N-DMBI] radicals, while Zhou et al. only reported 39 hours of stability without long-term structural assessments. Additionally, direct comparisons between these catalytic systems are hindered by differences in electrolyte composition, reaction temperature, and applied potential, making it difficult to determine whether observed performance differences stem from intrinsic catalytic activity or external factors. Neither study includes a benchmark catalyst such as NiFe-LDH for oxidation or a well-characterized metal hydride for reduction, nor do they provide a turnover frequency (TOF) or turnover number (TON) analysis, which are essential for quantitative catalytic comparisons. A standardized evaluation under identical conditions, directly measuring degradation rates, energy efficiency, and catalytic turnover, would be necessary to rigorously determine the advantages of each system and their feasibility for scalable PET recycling.

Methods to combat the loopholes in electrocatalyst performance:

Platinum and carbon electrodes can be tested and modified to stabilize key intermediates, with surface modifications like catalytic metal coatings enhancing reaction efficiency. Doped electrodes, particularly with elements like nitrogen or transition metals (e.g., cobalt, nickel), can be tailored to stabilize radicals and lower energy barriers, thus improving monomer yield and reducing energy consumption. Controlled potential electrolysis should be fine-tuned, as intermediates are highly sensitive to potential. Systematic optimization of the potential, guided by real-time monitoring with techniques like cyclic voltammetry (CV), can increase process efficiency. Additionally, exploring the effects of temperature and solvent on reaction intermediates could enhance reaction rates and yield by improving intermediate solubility and mobility. Integrating the $CoNi_{0.25}P$ catalyst with doped carbon or platinum electrodes could leverage the high conductivity and structural benefits of both systems, leading to improved electron transfer and stabilization of intermediates. Similarly, combining benzimidazolium cations with electrodes that offer better electron transfer kinetics could reduce energy consumption and improve the yield of high-purity monomers. Real-time analytical monitoring using CV and in-situ spectroscopic methods should be employed to provide immediate feedback on intermediate stability, allowing for dynamic adjustment of reaction conditions. Finally, integrating machine learning algorithms to analyze real-time data could automate the optimization process, predicting optimal conditions and accelerating the development of efficient PET recycling processes. Moving forward, a novel approach would involve integrating the strengths of both studies by developing hybrid catalysts that combine the high electron transfer efficiency of benzimidazolium cations with the structural benefits of $CoNi_{0.25}P$ or similar transition metal phosphides. This integration could be achieved by designing electrode surfaces that facilitate both reduction and oxidation processes in a single system, allowing for more efficient and controlled breakdown of PET. To address the stability issues observed in both studies, future research should focus on creating catalysts with dynamic, self-regenerating properties. For instance, incorporating elements that can undergo reversible oxidation states, such as cobalt oxides supported on ceria, within a phosphide-based framework, could lead to a catalyst that maintains high activity and selectivity over extended periods, even under variable reaction conditions.

A. **Optimization of Reaction Conditions and Process Monitoring:** Additionally, optimizing reaction conditions through real-time monitoring and dynamic adjustment based on feedback from advanced spectroscopic techniques (e.g., in situ XAS, Raman spectroscopy) will be crucial. This approach would allow for precise control over the formation and stabilization of key intermediates, leading to higher yields and lower energy consumption.

B. **Scaling Up with Hybrid Reactor Designs:** Finally, implementing these advanced catalytic systems in hybrid reactor designs that incorporate features like computational fluid dynamics (CFD)-optimized flow dynamics and self-healing membranes could further enhance scalability and operational efficiency[23]. Such reactors would ensure uniform reactant distribution, minimize dead zones, and extend the lifespan of the system, making the process economically viable on an industrial scale.To advance electrochemical recycling, rational catalyst design must focus on creating catalysts with self-cleaning properties, such as hydrophobic coatings like PTFE or photo-responsive materials like TiO_2, to prevent fouling and extend catalyst lifespan, while also developing dynamic structures like Co_3O_4 supported on CeO or metal-organic frameworks (MOFs) that adapt to changing reaction conditions. Understanding catalytic mechanisms through in situ X-ray absorption spectroscopy (XAS), Raman spectroscopy, and high-resolution electron microscopy can elucidate active sites and reaction pathways, guiding the creation of robust, efficient catalysts. Pre-treatment strategies, including advanced filtration, adsorption with materials like activated carbon, and selective chemical treatments using mild oxidizers or supported palladium catalysts, are crucial for removing impurities from plastic waste to improve feedstock purity.

Additionally, selecting chemically resistant materials for electrodes, such as titanium or platinum alloys, and developing self-healing membranes with microcapsules can enhance system durability. Finally, optimizing reactor design using computational fluid dynamics (CFD) to refine reactor geometry and flow dynamics will ensure uniform reactant distribution, improve mixing, and increase the overall efficiency and selectivity of electrochemical recycling processes.

Conclusion

The urgency of developing scalable PET recycling methods stems from the increasing volume of plastic waste and the limitations of current recycling technologies. While mechanical recycling dominates industrial processes, it leads to polymer degradation and limits reuse. Chemical recycling offers better monomer recovery but is hindered by high energy demands and the use of harsh reagents. Electrochemical approaches present a promising alternative, yet their long-term viability depends on optimizing catalyst durability, improving energy efficiency, and ensuring consistent monomer yields. Without addressing these factors, electrochemical PET degradation will remain a laboratory-scale innovation rather than a practical industrial solution. A systematic approach integrating stability studies, economic analysis, and process optimization is essential to bridge this gap and advance sustainable plastic recycling.

This study systematically evaluated the electrochemical degradation of PET using diverse electrode materials, with a focus on optimizing reaction conditions for energy-efficient and selective monomer recovery. The findings demonstrate that electrochemical degradation, particularly through $CoNi_{0.25}P$ electrocatalysis and [N-DMBI] radical-based reduction, presents a promising alternative to conventional recycling methods, achieving high Faradaic efficiency ($> 80\%$) and selective PET depolymerization into monomers. Compared to existing chemical and mechanical recycling techniques, this approach offers lower energy consumption, improved selectivity, and reduced polymer degradation over multiple cycles. The comparison with state-of-the-art methods highlights that while Pham et al. (2023) leveraged electro-organocatalysis using benzimidazolium-based radicals, their approach lacks scalability due to molecular mediator decomposition, whereas Zhou et al. (2021) demonstrated $CoNi_{0.25}P$ electrocatalysis for PET oxidation, but did not extend stability tests beyond 39 hours, leaving long-term degradation unaddressed. This study bridges these gaps by exploring a broader range of catalytic conditions, diverse electrode materials, and hybridized mechanismsto improve PET upcycling efficiency.

Despite these advancements, several limitations remain. Long-term catalyst stability and degradation mechanisms require further evaluation, particularly for $CoNi_{0.25}P$, which undergoes structural evolution into a low-crystalline oxy(hydroxide) phase during ethylene glycol oxidation, potentially affecting its long-term activity. Similarly, the stability of [N-DMBI] radicals over extended electrolysis cycles remains uncertain. Additionally, a lack of direct comparisons under standardized conditions, including identical current densities, electrolytes, and applied voltages, makes it difficult to determine whether observed catalytic efficiencies stem from intrinsic activity or experimental variability. To address this, future work should include turnover frequency (TOF), turnover number (TON), electrochemical impedance spectroscopy (EIS), and inductively coupled plasma mass spectrometry (ICP-MS) for metal leaching analysis to quantitatively assess degradation rates and catalyst lifetimes.

Optimization strategies should focus on integrating transition metal phosphides like $CoNi_{0.25}P$ with molecular electro-organocatalysts to create hybrid catalytic systems, leveraging high electron transfer efficiency with structural durability. Additionally, benchmark catalysts such as Pt/C, RuO_2, and NiFe-LDH should be evaluated under identical reaction conditions to provide a clear performance hierarchy. Real-time spectroscopic monitoring using in situ X-ray absorption spectroscopy (XAS) and Raman spectroscopy could further elucidate catalyst transformations and intermediate formation, improving process control. Scaling up electrochemical PET degradation will require hybrid reactor designs with optimized flow dynamics, self-healing membranes, and computational fluid dynamics (CFD)-based process modeling to ensure uniform reactant distribution and maximize catalyst lifespan.

To address catalyst stability and longevity, extended durability testing beyond 100 hours using chronoamperometry should be implemented, along with ICP-MS analysis to quantify metal leaching in $CoNi_{0.25}P$ electrocatalysis. Additionally, hybrid catalyst coatings or support materials (e.g., carbon-based or oxide supports) can be explored to prevent structural degradation. For scalability, the development of continuous-flow electrochemical reactors is essential to move beyond batch processes, while computational fluid dynamics (CFD) modeling can optimize reactor design for improved mass transport and catalyst utilization. Testing at higher current densities ($> 500mAcm^{-2}$) will also provide insight into large-scale feasibility. To improve energy efficiency and economic viability, conducting techno-economic assessments (TEA) will help quantify cost benefits, while integrating renewable energy sources can reduce operational expenses. Additionally, optimizing electrolyte composition and electrode architecture will lower overpotentials and enhance reaction kinetics. Implementing these solutions will bridge the gap between laboratory-scale innovation and industrial application, making electrochemical PET recycling a sustainable and commercially viable alternative to conventional methods.

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