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Circular Economy of Polymers – Electrochemical Recycling and Upcycling

by Chockkalingam Karuppaiah, Natasa Vasiljevic, Zheng Chen

Introduction

Our society depends on fossil-based resources for energy needs and feedstocks to make many synthetic organic materials, i.e., polymers. Synthetic polymers from fossil resources amount to over 440 million metric tons annually, and are expected to reach 700 million metric tons by 2030. About 20% of discarded synthetic polymers are recycled globally, about 25% are incinerated, and the balance are added to landfill.¹ While some energy is recuperated through incineration, the overall impact of today's linear economy principles of "make, use and mostly discard" approach impacts both local and global environment negatively. An alternative to this is a circular economy principle which aims at restructuring the way we think of design, manufacturing, consumption, and waste. By employing circular economy principles (Fig. 1), the feedstock for new synthesis will originate from discarded and recycled polymers after their useful life.

To be sustainable, our aim is to identify non-fossil feedstocks for synthesizing organic molecules, monomers and polymers. In addition to synthetic polymers, biopolymers such as cellulose and lignin, if not valorized appropriately, can end up in landfills generating methane through anaerobic decomposition.² Both end up contributing to greenhouse gas (GHG) emissions while losing valuable feedstock organic materials along the way. Thus, rethinking and expanding the circular economy principles to biopolymers has become paramount in addressing overall sustainability.

One of the main principles of the circular economy is prolonging the life of materials and products by upscaling them into new products with better performance and sustainable, simple reuse/recovery of components. Thus, to truly implement a circular economy, we need to advance from polymer recycling to polymer upcycling.

Most of the current methods to depolymerize plastic waste have been focused on pyrolysis-based methods.^{3,4} Those methods involve significant energy input, which if not generated through renewable sources, contributes to additional GHG release. In addition to that, achieving selective depolymerization with pyrolysis is challenging. Discarded polymers are typically mixtures of different types in terms of their molecular weight and nature. Discarded (recycled) plastic

often contains pigments and other additives which interfere with the chemical or pyrolytic approach, making it difficult to re-create the monomers and fine chemical feedstocks. The non-pyrolytic methods of polymer re/up-cycling involve homogeneous and heterogeneous catalysis and utilize chemical oxidizing and reducing agents for the process. Moreover, separating and treating the wastes from this process adds an additional step and overhead in the chemical recycling process. There is a need to identify novel techniques that are less harsh, selective, tolerant to contaminants and energy-efficient.⁵

The electrochemical recycling methods can offer a new economic prospect of generating monomers from waste polymers and new pathways to produce valuable chemicals. There has been progress in the synthesis of organic molecules through electrochemical reduction or oxidation.^{6,7} The electrochemical depolymerization reactions generally occur at milder conditions of ambient pressure and at temperatures below 100°C. The combination of improved selectivity, minimized usage of additional chemicals as oxidizing and reducing agents, and lower temperature operation can enable electrochemical approaches to close the loop on the circular economy of polymers.

Despite the opportunities, significant barriers remain before electrochemical recycling, and upcycling can be scaled up. One major challenge in the development is to address the difficulties associated with multi-functional polymers in which two or more of chemical groups such as aldehyde, alkyne, hydroxyl, carboxylic, ester etc. can co-exist. Without careful control, these functional groups will react at different voltage windows and generate a wide range of products during electrochemical depolymerization, which complicates the entire upcycling process with poor selectivity. Understanding the fundamental redox properties along with the innovation of cell and processes design could pave the way toward new practical applications.

Electrochemical Recycling of Synthetic Polymers

As mentioned above, common plastics such as polyolefin are often recycled by mechanical or chemical methods.^{3,4} The mechanical process requires clean and pure feedstock to be melted and remolded into a new product of the same type as that being recycled.³ Chemical methods can upcycle spent plastics by using a recycled monomers feedstock to synthesize other types of polymers, which can generate more valuable products. However, due to the high chemical stability of polyolefins, harsh conditions such as very high temperature as well as catalysis are required to deconstruct their original structure.^{4,8} In contrast to that, the electrochemical oxidation combined with potent oxidation mediators, e.g., Ag^{2+} ($E^0 = 1.98 \text{ V}$), Co^{3+} ($E^0 = 1.9 \text{ V}$), and Ce^{4+} ($E^0 = 1.7 \text{ V}$),⁹ have been reported as a new path to depolymerize polyolefins (Fig. 2).¹⁰ For example, using time-of-flight secondary ion mass spectrometry it has been identified that polypropylene and high-density polyethylene treated by electrochemical oxidation in the presence of Ag^{2+} ions can generate hydroxyl, carbonyl and carboxyl groups.⁹ These molecules with functional moieties can then be further processed to synthesize different types of polymers. These findings also suggest that the selectivity of such oxidation mediator-coupled electrochemical oxidation remains to be improved through cell chemistry design and/or process engineering, an important merit one should achieve to avoid complicated downstream chemical separation.

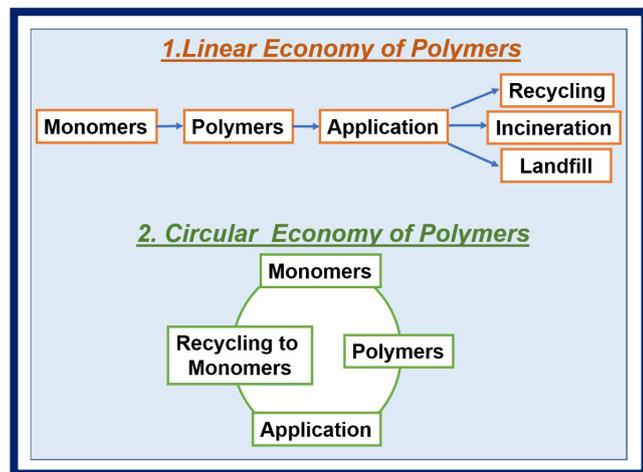


FIG. 1: Linear vs. circular economy of polymers.

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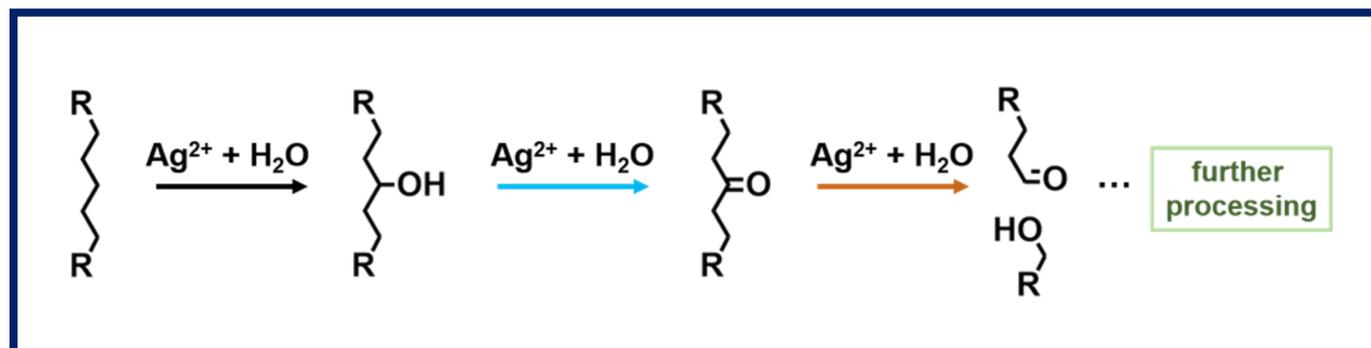


FIG. 2: Representation of an electrochemical oxidation of a polyolefin mediated by Ag^{2+} . Although speculative, the mechanistic schemes outlined above account at least partially for the surface electrochemical functionalization of HDPE, principally generate carbonyl and carboxylic acid fragments, with evidence for hydroxyls. These would be produced by oxidative attack at the $-\text{CH}_2-$ moieties, resulting ultimately in chain scission.^{9,10}

Other polymers (e.g., polyesters, amides) that contain relatively fragile linkages offer a better opportunity for electrochemical upcycling. For example, in a batch reactor using 1:1 methanol/water solution as the electrolyte, electrolysis of polyethylene (terephthalate) (PET) at 2.2V produced a yield of 17% of terephthalic acid after the one-hour operation.¹¹ By contrast, only 0.5% of terephthalic acid can be produced in 0.1M NaCl solution under the same voltage.¹¹ It is evident that improving the solubility of both the plastic and the upcycled product represents an important direction to pursue when designing electrolysis cells for upcycling. In addition, as compared in Table I, although the chemical upcycling process remains advantageous in terms of the product yield (in the batch, microwave reactors), one should note that the electrochemical method avoids the use of corrosive solutions that may solve a significant challenge in the scaling of the polymer recycling process. For electrochemical upcycling to play a more important role, electrode and electrolyte improvements will be essential tasks. Understanding the chemical interaction and charge-transfer processes in the three phase electrolyte/polymer/electrode interface may create critical knowledge to better design electrochemical depolymerization systems.

It should be noted that besides chemically simple polymers, any real plastic waste stream will consist of a diverse range of polymers with complex compositions. It may be possible to design a cascade electrochemical upcycling that treats each polymer component by a step-by-step approach, if the earlier products can be easily removed before electrochemical reactions move to the next step. However, a desirable and selective oxidation or reduction of one type of polymer may interfere with other polymers, which poses further challenges on achieving overall high selectivity of the entire stream. As such, effective pre-separation of mixed waste plastics will be a valuable step before an effective electrochemical upcycling can be applied to chemically similar polymers.

Electrochemical Recycling of Biopolymers

Owing to the strong inter-molecular and intramolecular hydrogen bonding, traditional methods of upcycling of biopolymers include the use of microbial processes (such as the use of fungi), use of the acidic environment, use of inorganic salts such as ZrCl_2 , CrCl_3 and/or the use of high temperature.^{12,13} These approaches have the downside of poor selectivity, the need for additional purification steps and can be energy-intensive. Electrochemical upcycling of biopolymers has attracted attention to potentially address these disadvantages through innovations in materials and electrochemical engineering.

Aqueous electrolytes offer inherent environmental advantages for chemical processing. The downside of the aqueous system is the faradic efficiency loss due to oxygen evolution. Similar to other electrochemical systems with gas evolution as a parasitic reaction, selecting an electrode material that has high overpotential for that parasitic reaction has been employed. Meng et al.¹⁴ used PbO_2 on Pb, with sulfuric acid as the electrolyte to oxidize cellulose. In addition to avoiding oxygen evolution, *in-situ* generation of hydroxyl radical and sulfate radical helped enhance the break up of inter-molecular and intra-molecular hydrogen bonding. After this depolymerization, further chemical reactions can be carried out to convert to fine chemicals that can be used as feedstock.

One of the proven methods in electrocatalysis is the use of mediators to widen the electrode materials selection. In the case of biopolymers, the type of mediators used will depend on the specific reaction. For example, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) can be used as a mediator for the oxidation of primary hydroxyls of cellulose. However, it is not strong enough to abstract benzylic hydrogen of lignin type alcohols during lignin oxidations.

Table I. Comparison of PET depolymerization using chemical and electrochemical methods.

Reaction #	Conditions	Reaction time	Terephthalic Acid Yield%
1 ^a	Water, 0.1 M NaCl, -2.2 V	60 min	0.51
2 ^a	50% MeOH in water, -2.2 V	60 min	16.9
3 ^b	MeOH, 85 °C	13 min	65
4 ^b	MeOH, 85 °C	40 min	65

a. Reactions at room temperature (21 °C), for 1h in a batch electrolysis H-Cell divided by a coarse ceramic frit at controlled potential against a single-junction Ag/AgCl reference electrode. Yield of terephthalic acid was obtained after the acidic workup of the cell contents.

b. Reactions were run in 20 mL CEM GlassChem vessels equipped with magnetic stir bars charged with 14 mL solvent and 10 mg end-use PET and 3.75 M NaOH with a maximum power of 1000 W.¹¹

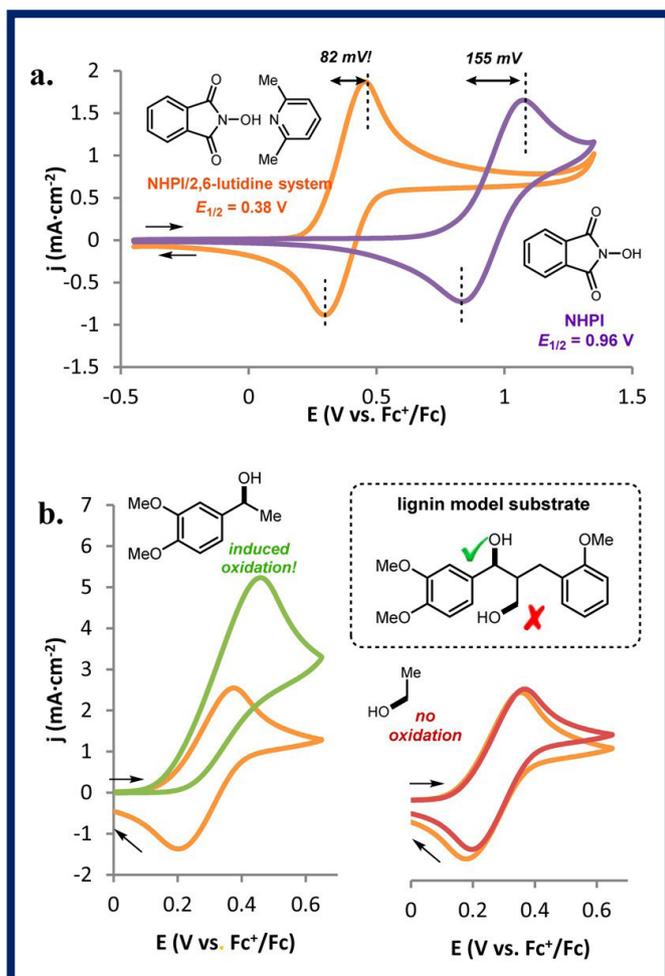


FIG. 3: Redox behavior of NHPI/2,6-lutidine catalyst and oxidation optimization. Cyclic voltammograms (CVs) at 50 mV/s of a 0.1 M NaClO₄ acetonitrile solution containing (a) 10 mM of NHPI (purple line), after addition of 10 mM of 2,6-lutidine (orange line), and (b) after addition of 100 mM 1-(3,4-dimethoxyphenyl) ethanol (green line) or 100 mM of ethanol (red line).¹⁵

To depolymerize lignin through electrooxidation, Bosque et al.¹⁵ used hydrogen atom transfer mediators based on N-hydroxyphthalimide (NHPI) with the addition of 2,6-Lutidine. The addition of Lutidine helped improve reversibility and decrease the oxidation potential (Fig. 3). The most common solvent and electrolyte systems for electro-oxidation have been either aqueous or organic systems. One of the new classes of electrolyte system that has been used in organic electrosynthesis is based on ionic liquids.¹⁶ Typically water is considered an impurity in these systems as it impacts the stable potential window in which oxidation can be carried out. Nevertheless, in the case of depolymerization, water is added intentionally to create hydroxy radical and peroxide *in-situ* within the ionic liquid system, leading to significantly improved depolymerization efficiency of lignin.¹⁷

Investigations in the depolymerization and upcycling of biopolymers also included engineering approaches based on the understanding of the mechanisms. One of the critical aspects that need to be optimized is the mass transport of the polymer. Approaches to address this include optimization of electrode morphology and removal of products generated.^{18,19} Stiefel et al.¹⁸ studied various morphologies of electrodes and reported the increase in the fraction of molecular weight reduction, with increase in volumetric mass transfer coefficient, tailored through increase in surface area and porosity. Removal of generated products has been a time-tested way to improve the mass transport of reactants to the surface of the electrode. Implementation of this was investigated in the depolymerization of biopolymers through two techniques, one with a nano filtration

approach using a membrane¹⁸ and the other with an anionic resin.¹⁹ Permeation through the nanofiltration membrane predominantly contains oxidized lignin, and the retentate containing unoxidized lignin can be recirculated. In the case of product separation with an anionic resin, the separation was carried out through the ionic and van der Waals interaction of generated product, vanillin, with the anionic resin.¹⁹ The product separation method not only helped with reducing the mass transport resistance but also helped avoid the over-oxidation of the generated product.

Summary and Outlook

Electrochemical pathways provide numerous advantages over chemical pathways in upcycling polymers. They enable carrying out the reaction under milder conditions of temperature and pressure. The use of electrons as redox agents helps avoid expensive and complicated additional purification of added oxidizing or reducing agents. Inherent shortcomings associated with the electrochemical approach may be addressed by innovations in: (i) efficient solubilization and mass transport of polymer to the electrode; (ii) improving selectivity through optimization of redox mediator; (iii) optimizing the extent of reaction through electrochemical reaction engineering; and (iv) effective combination of electrochemical, photochemical and thermochemical approaches to maximize efficiency and yield. Doing so will convert this problem into tremendous environmental and economic benefits, opening up a plethora of opportunities for the electrochemical community to contribute to a sustainable way of living.

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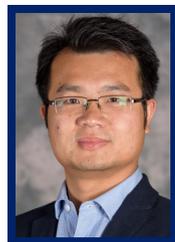
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