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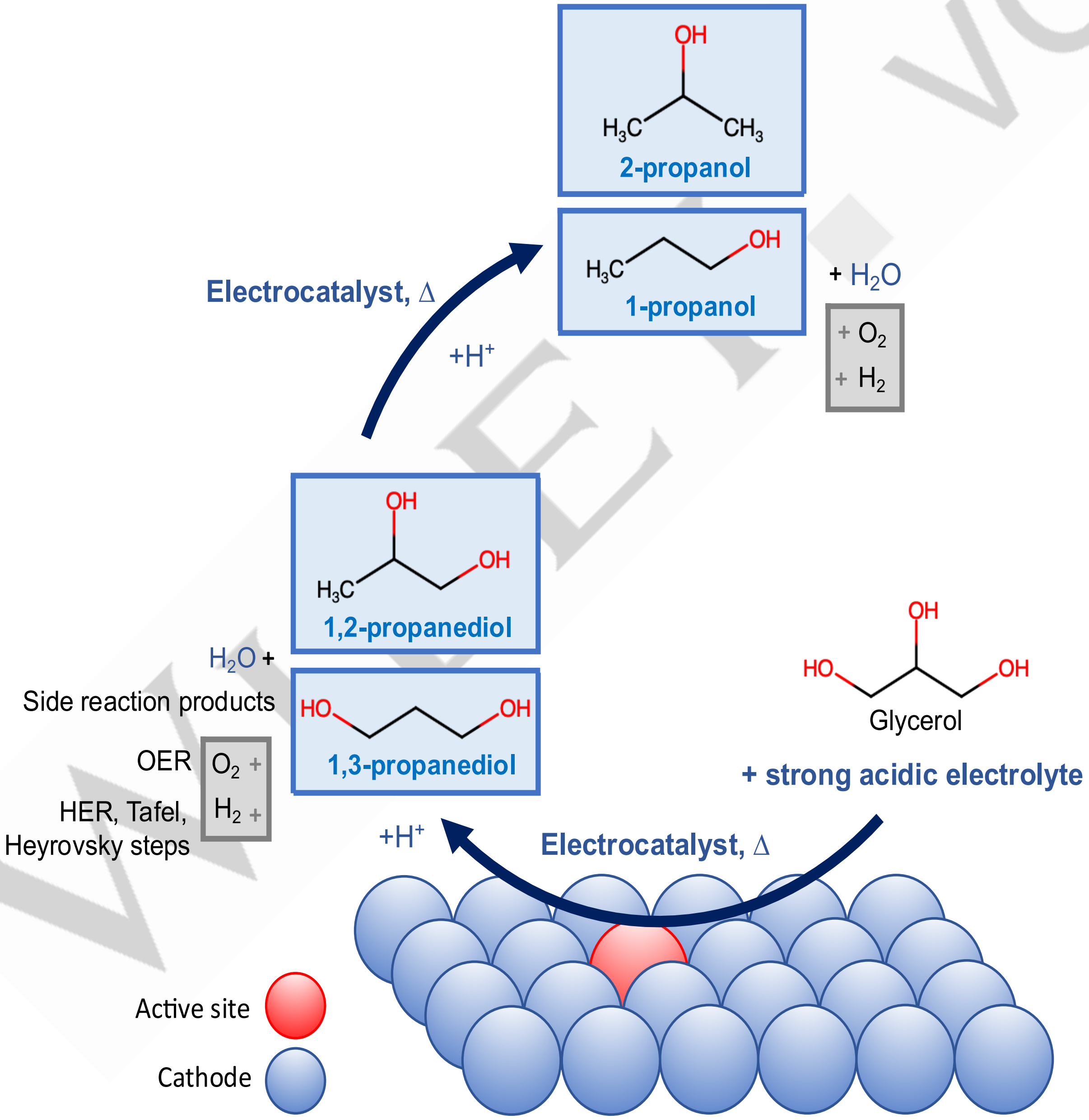
# Electrochemical Valorization of Glycerol via Electrocatalytic Reduction into Biofuels: A Review

Muhammad Harussani Moklis, Cheng Shuo, Sasipa Boonyubol, and Jeffrey S. Cross*[a]



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**Abstract:** Electrochemical conversion of underutilized biomass-based glycerol into high-value-added products provides a green approach for biomass and waste valorization. Plus, this approach offers an alternative to biofuel manufacturing procedure, under mild operating conditions, compared to the traditional thermochemical routes. Nevertheless, glycerol has been widely valorized via electrooxidation, with lower-value products generated at the cathode, ignoring the electroreduction. Here we study and establish a review of the efficient glycerol reduction into various products via the electrocatalytic reduction (ECR) process. This review has been built upon the background of glycerol underutilization and theoretical knowledge about the state-of-the-art ECR. The experimental understanding of the processing parameter influences towards electrochemical efficiency, catalytic activity, and product selectivity are comprehensively reviewed, based on the recent glycerol ECR studies. We conclude by outlining present issues and highlighting potential future research avenues for enhanced ECR application.

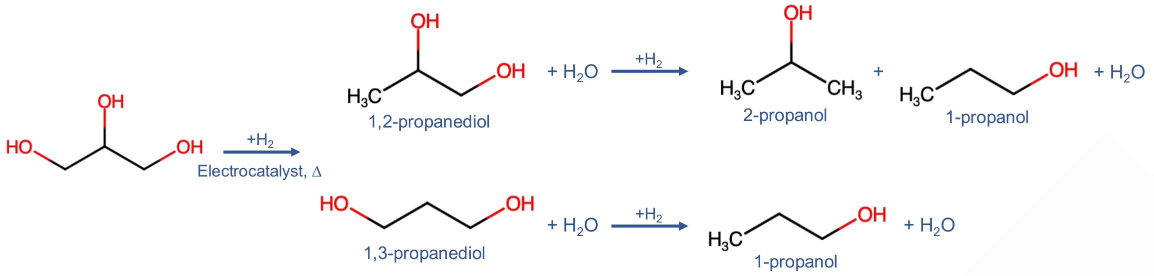
## 1. Introduction

The development of clean and green energy resources, including solar, wind, hydrogen, and bio-based energy, has attracted much attention due to their unique characteristics of an environmentally friendly approach to energy generation, robust and rapidly becoming cheaper in coming years [1], especially during this period of global environmental pollution, rising greenhouse gas (GHG) emissions, and critical energy crisis. Biofuel is an attractive carbon-neutral clean energy carrier, produced from renewable resources via sustainable practices with lower GHG emissions than the current utilization of conventional petroleum-based fuels [2]. By 2021, according to the International Energy Agency (IEA), the global biofuel demand reached 4 exajoule (EJ) –160 billion liters– which was dominated by the production of biodiesel (1.76 EJ), and bioethanol (2.16 EJ) [3]. Aligning with the Net Zero Scenario, in 2030, it is expected that the demand for these biofuels increased drastically by 265% (to 6.41 EJ) and 255% (to 7.68 EJ), respectively. These positives hinge on several significant factors of reduced manufacturing cost, support by governmental policies, and diversity in sustainable feedstock supplies-including waste and edible bio-oils.

Glycerol is formed as a by-product during the transesterification reaction of biodiesel production as well as produced in other oleochemical industries. According to the data from IEA, global biodiesel generation is more than 50 billion liters in 2021, where 5 billion liters of glycerol were produced [3]. Thus, currently, the rapid development of the biodiesel industry has resulted in a significant surplus of glycerol on the world market. Considering that glycerol is an abundant waste product [4,5] and that it is the second simplest sugar molecule [6], glycerol upgrading to valuable products has a significant impact on the biodiesel economy [7] whereas, according to Nomanbhay et al. [8], major biodiesel producers are currently refining the crude glycerol to pure glycerol through expensive purification processes. The study of new and low-cost processes for crude glycerol upgrading is paramount.

The economic viability of crude glycerol upgrading can be improved by its valorization into high-value-added biofuels such as propanols. As mentioned by Li et al. [9], n-propanol can be used as an engine fuel due to its high octane number of 118, its greater carbon structure, and higher calorific value, thus, propanol is a better alternative fuel than other alcohol subgroups like methanol and ethanol. Plus, propanol has a larger energy density and flashpoint compared to methanol and ethanol. Although it has a higher heat of vaporization than diesel, its low autoignition temperature will result in a shorter ignition delay than other alcohols [10]. However, the potential application of propanol as a substitute fuel for vehicle engines is yet constrained by the higher manufacturing cost and high reliance on fossil resources–conventionally via ethylene hydroformylation and propanal hydrogenation. Hence, few experimental studies on propanol have been conducted recently, and research on cheap propanol manufacturing is underway.

Recently, glycerol has been considered as an alternative candidate of biofuel resources for the electrochemical valorization process, into propanol (see Scheme 1), along with other upgrading reaction-thermochemical (hydrogenolysis, catalytic pyrolysis, and reforming), etherification, and biochemical (via fermentation) routes [11]. According to our previous publication [11], summarized in Table 1, we could conclude that electrochemical pathway is more superior than the others in terms of performance, complexity and economic-wise. There has been increasing commercial demand in electroreduction, also known as electrocatalytic reduction (ECR). Due to its greener, and simpler manufacturing setup, the utilization of this method is very promising and offers several more advantages–higher product selectivity, no safety concerns due to ambient processing environment, has better catalyst stability and reusability, generate clean energy–compared to the traditional heterogenous catalytic hydrogenation process. Since it utilizes an electron to serve as a redox reagent instead of potentially dangerous chemical oxidants and reductants, it is frequently seen as an environmentally friendly procedure. Plus, it provides significantly high energy efficiency and is capable of being operated at mild conditions–ambient temperature and pressure, without the requirement of an external power source for the heating system [12,13] as well as an external hydrogen supply [14].



**Scheme 1.** Illustration of potential electrochemical routes of glycerol into propanol at cathode electrode under the influence of electrocatalyst and heat energy from elevated process temperature.

**Table 1.** Comparison of current glycerol reduction pathways [11,15,16].

| Pathways | Parameter performances | | | | | | Energy type | Energy consumption |
|---|---|---|---|---|---|---|---|---|
| | Temperature | Pressure | Time | Catalyst | Reductant sources | Side reactions | | |
| Bio-chemical (microbial fermentation) | Medium (70-160 °C) | Mild (101.3 kPa) | Long (Few days) | Microbes/ pure culture | Microbes, organic co enzyme – NADH, FADH2 | Organic acid formation | Bio-chemical energy | High energy demand for enzymes (low energy input – metabolic pathway and enzymatic reactions) |
| Thermo-chemical (pyrolysis, catalytic hydrogenolysis, steam reforming) | High (>300 °C) | High (>15 MPa) | Short (Few minutes) | Metals/ zeolites | External hydrogen gas supply | Carbon deposition, $CO_2$ generation | Electrical and thermal energy | High (heat, external hydrogen supply and pre-treatment requires higher energy input) |
| Electrochemical reduction | Mild (25-80 °C) | Mild (101.3 kPa) | Medium (Few hours) | Metals/ carbon | Electrons, generated $H^+$ ions | HER, Tafel and Heyrovsky reactions | Electrical energy | Low (energy input is to provide the necessary electrons for the reaction) |

*NADH – nicotinamide adenine dinucleotide (NAD) + hydrogen (H); FADH2 – flavin adenine dinucleotide; HER – hydrogen evolution reaction.

For instance, a temperature of above 200 °C is needed to produce about 85% selectivity of 1,2-propanediol (1,2-PDO) via thermochemical approach of hydrodeoxygenation reaction whereas higher selectivity of 1,2-PDO is yieldable at milder process temperature via electrochemical approach–86% selectivity at 80 °C [17], 85% selectivity at 27 °C [18] and 89% selectivity at 27 °C [19]. The electrochemical process involves two half-reactions, called redox reactions (reduction and oxidation) which can be optimized by altering its main parameters to produce specific end-products. Thus, the control of electrocatalytic reduction reaction and its selectivity is majorly influenced by the nature of the electrode materials/electrocatalysts, electrolyte pH, reaction temperature, applied potential, and current density which can be tuned and optimized for better efficiency [20–22]. Despite that glycerol electroreduction is easily achieved at high potentials [21], establishing an electroreduction setup with improved conversion and selective reaction is still a knowledge gap.

To the best of our knowledge, successful ECR conversions of glycerol are rather still scarce which mainly due to the fact that this approach is a relatively newer approach compared to other well-established glycerol conversion pathways–aforementioned hydrogenolysis and catalytic pyrolysis [5,23], plus, there are still a few technological challenges due to the lack of knowledge regarding its complex reactions and how to control them [24] – to selectively reduce the glycerol while preventing further redox reaction can be very challenging. In addition, most of the published review articles only emphasized the electrooxidation reaction of glycerol and its relevant research toward an efficient practice [5,23,25,26] to synthesize various oxygenated chemicals. According to the literature, glycerol electrooxidation studies were mainly motivated in generating anodic oxidation-derived chemicals (such as dihydroxyacetone (DHA) (~US$30/kg) [27], glyceraldehyde (GA) (~US$10/kg) [28], glyceric acid (~US$3/kg) [29] and lactic acid (~US$14/kg) [30]) which have higher economic value as compared to several cathodic reduced products which includes acetone (~US$1.04/kg), 1,3-PDO (~US$4.5/kg), 1-POH (~US$1.15/kg), 2-POH (~US$0.01/ton) and propane (~US$0.7/kg) [31]. Houache et al. [32], Talebian-Kiakalaieh et al. [26], and Kwon et al. [33], on the other hand, highlighted the latest studies related to electrocatalyst selection and characterization of glycerol oxidation. Unfortunately, the published studies do not provide sufficient information on the working principle of glycerol electroreduction. Howbeit, glycerol ECR has a promising potential in waste valorization field as it offers facile greener deoxygenation process. Plus, the simple processing setup will lead to its easy integration with biodiesel plants, hence, lead to cost savings for transporting and storing the waste glycerol and improved economic viability of the overall biodiesel production process. Hence, a thorough diagnosis of glycerol electroreduction conversion to functional chemicals is paramount to be discovered.

In this review, the main aim is to discuss recent novel breakthroughs in the electrochemical reduction of glycerol which will lead to major improvements in upgrading oxygenated compounds into biofuels. In addition, the review addresses the critical knowledge gaps for enhancing high product selectivity, yield, and conversion which are influenced by the control of its major process parameters. A significant spotlight is placed on the electroreduction conversion which will provide knowledge towards attaining excellent electrocatalytic performance at a mechanistic level.

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Jeffrey S. Cross received his Ph.D. in Chemical Engineering in 1992 from Iowa State University, Ames, Iowa, USA. In 1993, he received a US National Science Foundation Post-doc fellowship at the National Institute for Research in Inorganic Materials, Tsukuba, Japan and later worked at Fujitsu Laboratories Ltd. in Atsugi Japan, 1994-2008. In 2008, he joined Tokyo Tech and opened the Cross laboratory in 2016 in the School of Environment and Society. His lab conducts research on biofuels, $H_2$ gas separation, energy policy, and educational technology.

## 2. Electrocatalytic Reduction/ Deoxygenation of Glycerol

Electrocatalytic reduction (ECR) describes the transformation in the electrochemical circuit of losing protons and gaining electrons to selectively remove oxygen (electro deoxygenation [34]) and/or add hydrogen functionality (electrochemical hydrogenation [35]) to the oxygenates. In a simple/single ECR cell of glycerol ($C_3H_8O_3$) as shown in Figure 1, which is undivided with any electrolyte membrane and in a batch system, there will be two main reactions (or called half-cell reactions) occur at the cathode (Reaction 1 and 2) and the anode (Reaction 6) which majorly contributed to the electroreduction of glycerol, acts as the electrolyte. Generally, water or acidic medium oxidation happens at the anode, as shown in Reaction 6, resulting in the production of oxygen gas, and protons. The electrons liberated via the electrooxidation reactions at the anode will travel via the external circuit to complete the loop [36]. In the interim, as illustrated in Figure 1, the generated protons of hydrogen ions ($H^+$) migrate via the electrolyte (aqueous medium) from the anode to the cathode. This migration is propelled by the natural reaction of the negatively charged electrode to attract cations towards it [37]. Next, they conduct reduction to synthesize surface-bound atomic hydrogen (H*) [35]. The adsorbed H* might interact with the oxygenated/reduced molecules of interest, which induce ECR. Alternatively, the hydrogen atoms might rejoin and desorb, either through the hydrogen evolution reaction (HER) or other side reactions – Tafel reaction (Reaction 4) and Heyrovsky processes (Reaction 5) [38]. Thus, the HER and ECR sub-reactions tend to compete, which reduces the net electrochemical efficiency (EE) of the whole reaction [4]. From Table 2, we can observe that the product selectivity in a single cell also much lower (~50%) than the double-compartment cell due to the abovementioned high competition between ECR with other parasitic side reactions.

At the cathode,
Main reaction:

$$C_3H_8O_3 + 2H^+ + 2e^- \rightarrow C_3H_8O_2\ (Reduction\ product) + H_2O \quad (1)$$

$$C_3H_8O_2 + 2H^+ + 2e^- \rightarrow C_3H_7OH\ (Reduction\ product) + H_2O \quad (2)$$

Side reaction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

$$2H^* \rightarrow H_2 +^* \quad (4)$$

$$H^* + H^+ + e^- \rightarrow H_2 +^* \quad (5)$$

At the anode,
Main reaction:

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \qquad (6)$$

Side reaction:

$$C_3H_8O_3 \rightarrow C_3H_7O_3\ (Oxidation\ product) + H^+ + e^- \qquad (7)$$

Net reaction:

$$C_3H_8O_3 \rightarrow C_3H_7OH + O_2 \qquad (8)$$

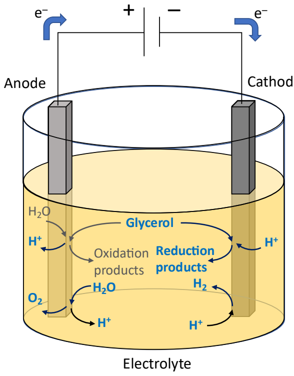


**Figure 1.** Schematic of simple ECR single cell.

Below, other than a simple single cell, a divided cell or H-type cell or also called a two-compartment electrochemical cell (see Figure 2) is recently utilized with either an anion-exchange membrane (AEM) and proton-exchange membrane (PEM)/cation-exchange membrane (CEM). The current most utilized CEM, which is feasible for electroreduction reaction, is the Nafion-117 membrane. Its high permeability towards cations–$H^+$–while less permeable towards the minimal exchange of solvent and neutral molecules favour its broad utilization [14,17,19,39–41]. Migration of ions through anolyte to catholyte is very imminent in this setup. It enables complete redox catalysis as well as ensures high conductivity and low applied voltage between both electrodes in the system [42]. Generally, based on Figure 2, electrolysis of water at the anode via electrooxidation reactions will generate hydrogen protons ($H^+$), similar to a single cell, but then, the protons further migrate through the membrane to catholyte region due to the major difference in electrode potentials. The separation between anode and cathode by membrane leads to enhanced reduction product selectivity (~90%) [17,19] due to the fact that the oxidation products in anolyte cannot pass through the membrane and avoid any side reaction. This approach, thus, allows improved hydrodeoxygenation or hydrogenation reactions to happen in the catholyte.

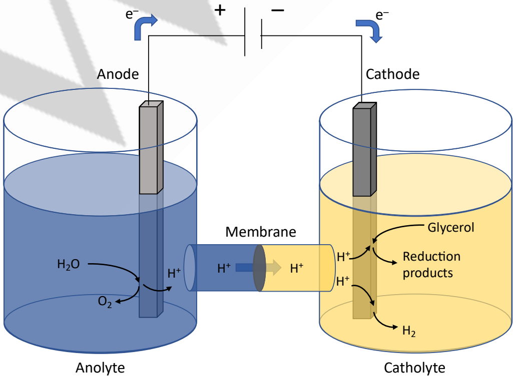


**Figure 2.** Schematic illustration of the ECR divided cell (or also called H-type cell).

In another work related to the electrochemical conversion of bio-oil-containing oxygenated compounds, the utilization of advanced divided cells with the double membrane of AEM and PEM has been introduced [14,35,43]. Lister et al. [14] discussed, within the double membrane cell (DMC), dissociated $H^+$ protons and/or water are absorbed by the cathode in two main processes: (i) the hydrogenation of organic molecules, and (ii) the HER (a parasitic side reaction) that is unavoidable, as discussed earlier. Protons generated in the catholyte via reduction cause the catholyte pH to rise while the concentrate pH (at the middle of both membranes) falls due to the accumulation of protons from the anode and anions from the catholyte. This happens as smaller and uncharged organic molecules can pass through the membrane via osmosis. In a single membrane cell, these molecules will lead to various minor reactions. Thus, it is advantageous to have a double membrane, to separate the catholyte from the anolyte, where small acids, organic neutrals, and other anions from bio-oil are removed from the concentrated section. Hence, it leads to a better reaction performance. Nevertheless, according to Rausch et al., the utilization of high-cost membranes within two- or more compartment cells hinders its application in large-scale industries [44]. The membranes are irreversible and have shorter lifetimes due to their degradation from interaction with the reactive species formed within the electrolyte [45]. Thus, the majority of the published studies utilized undivided cells due to their facile design and low manufacturing cost, however, it demonstrated lower PDOs selectivity (~50%) [46,47]. Bard et al. [48] explained that the electrochemical reduction of hydroxyl groups is extremely challenging to be achieved effectively due to its negative reduction potentials.

Overall, ECR stands out as a possible option in this context due to its ability to stimulate the electrochemical synthesis of catalyst surface-bound atomic hydrogen at mild temperature and atmospheric pressure. The utilization of electrolysis will further inhibit the requirement for an external hydrogen supply for catalytic hydrotreating and deoxygenating reactions due to the internally produced hydrogen supply. An inevitable by-product known as internally produced $H_2$ gas may be employed in downstream hydrotreating to further hydrogenate the feedstocks. Plus, the generation of oxygen molecules (O2) at the anode can be further utilized as a pure oxygen gas supply, as illustrated in Figures 2 and 3. In addition, the polymerization problems brought on by high processing temperatures in conventional hydrothermal techniques are likewise reduced by these mild process conditions. This also offers an improved overall electrochemical performance. Based on the literature, to achieve high conversion and selectivity, it is essential to tune the kinetics of ECR by major reaction parameters optimization–process temperature, applied potential/current, electrolyte pH, and electrocatalyst nature–which will be further discussed after this. The effects of these parameters toward ECR performance will be primarily illustrated deliberated using its conversion (GC) values, product yield (PY), each product selectivity (PY), electrochemical efficiency (EE) and coulombic efficiency (CE) (also called faradaic efficiency or current efficiency), as follows.

$$GC\ (\%) = \frac{Mole\ \ of\ reactant\ consumed}{Total\ mole\ of\ initial\ reactant} \times 100$$

$$PY\ (\%) = \frac{Mole\ of\ product}{Mole\ of\ initial\ reactant} \times 100$$

$$PS\ (\%) = \frac{Mole\ of\ specific\ product}{Total\ mole\ of\ liquid\ product} \times 100$$

$$EE\ (\%) = \frac{Number\ of\ electron\ to\ generate\ product}{Total\ electron\ \ used\ in\ the\ process} \times 100$$

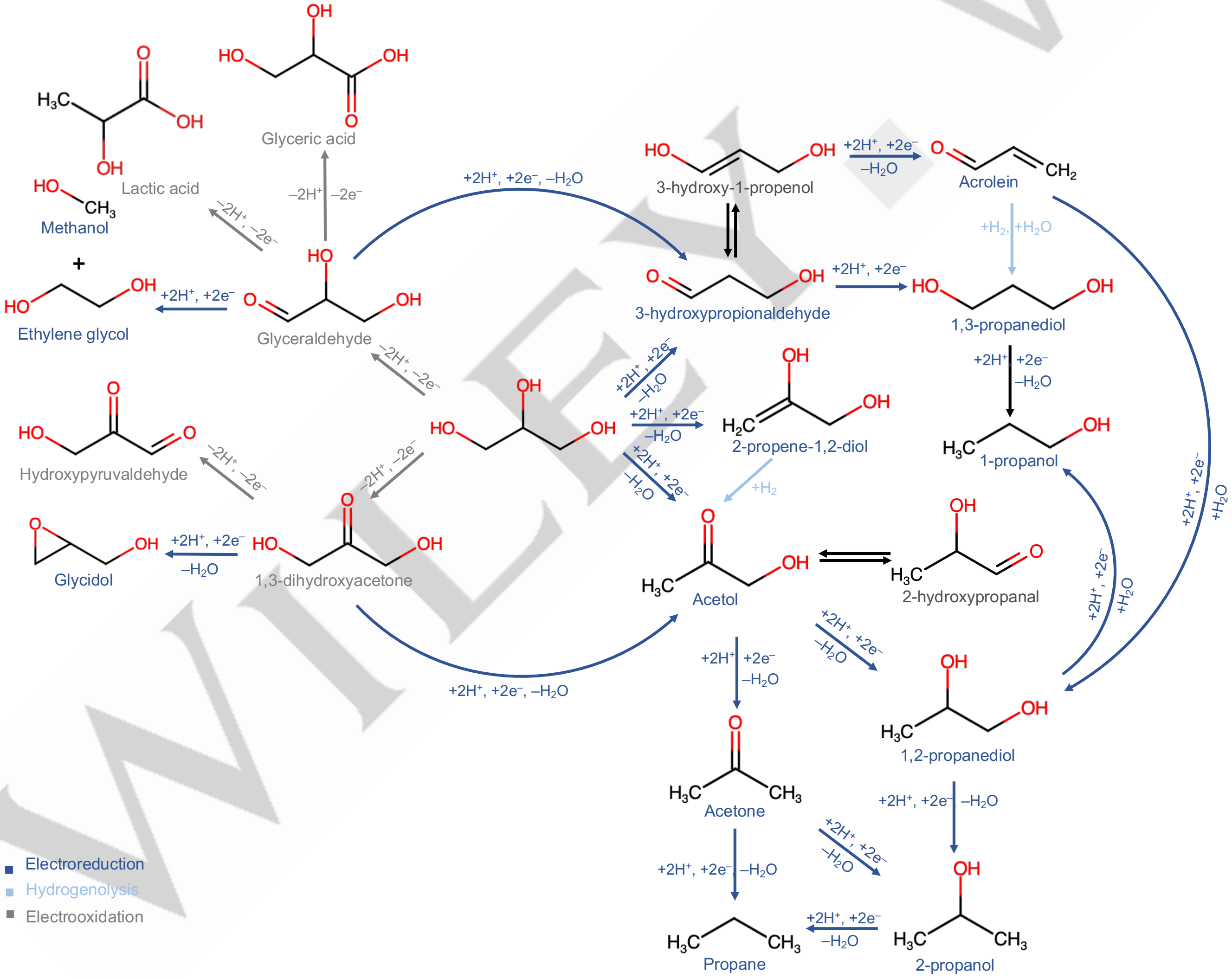
$$CE\ (\%) = \frac{Total\ charge_{discharge}}{Total\ charge_{charge}} \times 100$$

On the other hand, throughout this study, we will standardize the use of EE term for both EE and CE as both have similar meaning of indicating the maximum efficiency for an electrochemical cell.

## 3. Current Works on Glycerol ECR

Selective electroreduction of crude and pure glycerol is still far from being optimal for low-cost production. Nevertheless, ECR is a viable alternative for boosting crude glycerol value and avoiding post-production disposal and purification expenses [43]. Glycerol ECR is an economically feasible synthesis used to generate high-value-added chemicals (including acetol, acrolein, acetone, 1,2- and 1,3-PDO, etc.) and biofuels (n- and 2-propanols), as shown in Scheme 2.

Recently, less attention has been given to electroreduction pathways, compared to oxidation, albeit it comprises various significant valorization reaction –hydrogenolysis, hydrodeoxygenation, and electro-deoxygenation– in the recent decade [4]. These specific reactions are significant in generating biofuels from crude glycerol, removing oxygen molecules from the compounds. Here, in Scheme 2, we map out various possible electrochemical reactions of glycerol that occurred within the electrochemical cell. Great focus has been given to the electroreduction transformation of glycerol into PDOs, propanol (POH), and propane, which mainly facilitated by the hydrogenation of $H^+$ ions produced at anode (Equation 6). It displays how deoxygenation of glycerol could be achieved under mild conditions via ECR.



**Scheme 2.** Possible pathways for electrocatalytic reduction (blue arrow) and electrooxidation (grey arrow) of glycerol in a single and double-compartment cell. In a single cell, both redox reactions happened, and products were mixed due to the absence of separating membrane. In double or more-compartment cells, only reduction products are generated within the catholyte.

A clear overview of recent proof-of-concept studies focusing only on the electroreduction of glycerol was presented in Table 2. We, thus, could observe the direct influence of various combination of major operating parameters which affects the feedstock conversion rate, yield, and selectivity of the electroreduction-derived products, which will be thoroughly discussed in the next section. For instance, several excellent papers on the electroreduction conversion of glycerol have been published recently. The study on glycerol electrocatalytic reduction reaction was started by Kongjao et al. [47] and demonstrated the electrochemical transformation of glycerol to PDO, POH, and propane. While, methodical proof-of-concept studies of the impact of process parameters–initial electrolyte pH, current density/voltage applied, the combination of electrocatalysts, the surface area of the electrode, and glycerol concentration-for this reaction were done by several other researchers [17–19,21,46,49].

According to Table 2, lower electrolyte pH along with Pt electrodes works well with higher current density applied in order to produce the highest conversion rate as well as better electroreduction efficiency. Recent works to investigate the relationship between electrolyte pH with the EE and product selectivity over conventional Pt electrodes have been successfully investigated by Hunsom and Saila [46] and Sauter et al. [49]. They both have consistently demonstrated that lower pH values of electrolytes favor a higher degree of electroreduction reaction. Whereas, studies on the effect of current density applied towards the electrolytic circuit have been demonstrated by James et al. [18], and Hunsom and co-researchers [21]. Interestingly, James et al. [18] have utilized non-noble metallic electrodes (iron (Fe), aluminum (Al), molybdenum (Mo), copper (Cu), nickel (Ni), tungsten (W), chromium (Cr), lead (Pb), zinc (Zn), etc.) along with Ti/$RuO_2$, as the working and counter electrodes, respectively.

Pt electrodes are still the main choice as electrocatalysts for redox reactions due to their robustness and high catalytic performance. However, Sauter et al. [49] studied the state-of-the-art impact of various non-noble metal-based electrocatalysts' nature on the electroreduction of glycerol, an effort to discover new alternatives for high-cost platinum-based electrodes. In their works, 11 types of metals have been introduced to be used as working electrodes to convert a dehydration product of glycerol, HDA, and acetone into PDOs and POHs, respectively, through selective ECR. More recently, Rahim et al. [19] and Lee et al. [17] demonstrated works using carbon black activated carbon electrodes under acidic conditions with improved selective reduction of glycerol. Lee et al. [17] also had done an important study by demonstrating enhanced PDO yield and selectivity under an elevated processing temperature of 80°C.

Yet, a proper fundamental study on this topic should be done by investigating the changes of electrocatalyst nature under elevated temperatures. This is because according to collision theory of thermodynamic, the temperature is proportional to the electrolysis reaction rate. Elevating the process temperature will increase the kinetic energy of the molecules within the electrolyte, thus, leads to a higher probability of the adsorbed molecules to acquire the necessary activation energy. Greater number of molecules with high kinetic energy makes them easier to interact with the surplus $H^+$ protons generated at the anode (Reaction 6). Plus, higher temperature might positively impact the exophilic nature of the electrocatalysts used [50,51]. However, a thorough study to explain this significant influence is needed, since Faraday's first law of electrolysis has theoretically neglected the dependent towards electrolysis temperature.

**Table 2.** Literature review on electrochemical reduction of glycerol.

| Feed | Cell types | Electrodes | | T (°C) | J (A/cm$^2$) | V (V) | Electrolyte pH and types | t (h) | ECR results | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Anode | Cathode | | | | | | EE (%) | GC (%) | Main product | PY (mole %) | PS (%) | |
| Glycerol | Single cell | Pt | Pt | 30 | - (4.5A) | 2 | pH 1 ($H_2SO_4$) | 6 | - | 30 | 1,2-PDO | 20 | - | [47] |
| | | | | | | | | | | | 1,3-PDO | 40 | - | |
| Glycerol | Single cell | Pt | Pt | 25 | 0.14 (4.5A) | - | pH 1 ($H_2SO_4$) | 13 | - | 100 | Acrolein | 33 | - | [46] |
| | | | | | | | | | | | 1,3-PDO | 25 | - | |
| | | | | | | | | | | | Acetol | 17 | - | |
| | | | | | | | | | | | Glycidol | 16 | - | |
| | | | | | | | | | | | 1,2-PDO | 5 | - | |
| | | | | | | | pH 7 ($Na_2SO_4$) | 24 | - | 76 | Glycidol | 18 | - | |
| | | | | | | | | | | | Acrolein | 14 | - | |
| | | | | | | | | | | | Acetol | 5 | - | |
| | | | | | | | pH 11 (NaOH) | 24 | - | 90 | Glycidol | 29 | - | |
| | | | | | | | | | | | Acrolein | 18 | - | |
| | | | | | | | | | | | Acetol | 16 | - | |
| Enriched crude glycerol | Single cell | Pt | Pt | 25 | 0.14 | - | pH 1 ($H_2SO_4$) | 17 | 75 | 100 | Glycidol | 48 | - | [21] |
| | | | | | | | | | | | Acrolein | 33 | - | |
| | | | | | | | | | | | Acetol | 12 | - | |
| | | | | | | | | | | | 1,2-PDO | 3 | - | |
| | | | | | | | | | | | 1,3-PDO | 3 | - | |
| | | | | | 0.24 | - | | 14 | - | 100 | Glycidol | 52 | - | |
| | | | | | | | | | | | Acrolein | 35 | - | |
| | | | | | | | | | | | Acetol | 15 | - | |
| | | | | | | | | | | | 1,2-PDO | 5 | - | |
| | | | | | | | | | | | 1,3-PDO | 2 | - | |
| | | | | | 0.27 | - | | 8 | - | 100 | Glycidol | 44 | - | |
| | | | | | | | | | | | Acetol | 15 | - | |
| | | | | | | | | | | | 1,2-PDO | 12 | - | |
| | | | | | | | | | | | 1,3-PDO | 0 | - | |
| | | Pt | Ti/ $RuO_2$ | 25 | 0.14 | - | | 17 | 35 | 43 | Glycidol | 14 | - | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | pH 1 ($H_2SO_4$) | | | | Acetol | 7 | - | |
| | | | | | | | | | | | 1,2-PDO | 4 | - | |
| | | Pt | SS | 25 | 0.14 | - | pH 1 ($H_2SO_4$) | 9 | 30 | 23 | Acrolein | 10 | - | |
| | | | | | | | | | | | Glycidol | 7 | - | |
| | | | | | | | | | | | Acetol | 6 | - | |
| | | | | | | | | | | | 1,2-PDO | 2 | - | |
| | | | | | | | | | | | 1,3-PDO | 2 | - | |
| HDA | Double cell | Pt | Fe | RT | - | –1.8 | pH 2 (NaCl/HCl) | 4 | 33 | - | 1,2-PDO | - | 85 | [49] |
| | | | Al | | | | | | 38 | - | 1,2-PDO | - | 85 | |
| | | | Mo | | | | | | 13 | - | 1,2-PDO | - | 48 | |
| | | | Cu | | | | | | 50 | - | 1,2-PDO | - | 34 | |
| | | | | | | | | | | | Acetone | - | 15 | |
| | | Pt | Cu | RT | - | –1.8 | pH 7 (phosphate buffer solution) | 4 | 12 | - | 1,2-PDO | - | 90 | |
| | | | Mo | | | | | | 11 | - | 1,2-PDO | - | 77 | |
| | | | Fe | | | | | | 10 | - | 1,2-PDO | - | 75 | |
| | | | Ni | | | | | | 7 | - | 1,2-PDO | - | 70 | |
| | | | W | | | | | | 8 | - | 1,2-PDO | - | 65 | |
| | | Pt | Cr | RT | - | –1.8 | pH 1.15 ($NaHSO_4$) | 4 | 2 | - | 1,2-PDO | -- | 60 | |
| | | | Fe | | | | | | 5 | - | 1,2-PDO | - | 40 | |
| | | | | | | | | | | | Acetone | - | 17 | |
| | | | Mo | | | | | | 3 | - | 1,2-PDO | - | 27 | |
| | | | | | | | | | | | Acetone | - | 12 | |
| Acetone | | Pt | Fe | RT | - | –1.8 | pH 7 (NaCl) | 4 | 15.3 | 82 | 2-POH | - | 79 | |
| | | | | | | | pH 2 (NaCl/HCl) | | 26.4 | 80 | 2-POH | - | 87 | |
| | | | | | | | pH 7 ($Na_2SO_4$) | | 9.4 | 41 | 2-POH | - | 80 | |
| | | | Mo | | | | pH 7 ($Na_2SO_4$) | | 12.9 | 43 | 2-POH | - | 75 | |
| | | | | | | | pH 2 (NaCl/HCl) | | 19.4 | 67 | 2-POH | - | 75 | |
| Glycerol | Double cell | Pt | CBAC | 80 | - (2A) | - | pH 1 ($Na_2SO_4$/ Amberlyst-15) | 8 | - | 74 | 1,2-PDO | - | 86 | [17] |
| | | Pt | CBD | 80 | | | | | - | 88 | 1,2-PDO | - | 68 | |
| | | Pt | Pt | 80 | | | | | - | 67 | 1,2-PDO | - | 61 | |
| Glycerol | Single cell | Ti/ $RuO_2$ | Pb | 25 | - | –1.8 | pH 1 (HCl) | 10 | - | 33 | GA | - | 50 | [18] |
| | | | | | | | | | | | 1,3-PDO | - | 10 | |
| | | | | | | | | | | | Acetol | - | 15 | |
| | | | | | | | | | | | 2-POH | - | 2 | |
| | | Ti/ $RuO_2$ | Zn | 25 | - | 2.5 | pH 7 (NaCl) | 10 | - | 6 | GA | - | 30 | |
| | | | | | | | | | | | 1,3-PDO | - | 52 | |
| | | | | | | | | | | | Acetol | - | 20 | |
| | | | | | | | | 24 | - | 23 | GA | - | 8 | |
| | | | | | | | | | | | 1,3-PDO | - | 30 | |
| | | | | | | | | | | | Acetol | - | 24 | |
| | | | | | | | pH 1 (HCl) | 10 | - | 76 | GA | - | 8 | |
| | | | | | | | | | | | 1,3-PDO | - | 4 | |
| | | | | | | | | | | | Acetol | - | 10 | |
| | | | | | | | | | | | 2-POH | - | 4 | |
| | | | | | | | | | | | Acetone | - | 2 | |
| | | Pt | Pb | 25 | - | –1.8 | pH 1 (NaCl/HCl) | 10 | - | 50 | GA | | 6 | |
| | | | | | | | | | | | 1,3-PDO | - | 20 | |
| | | | | | | | | | | | Acetol | - | 5 | |
| | | | | | | | | | | | 2-POH | - | 2 | |
| | | Pt | Zn | 25 | - | –1.8 | pH 1 (KCl/HCl) | 10 | - | 45 | GA | - | 2 | |
| | | | | | | | | | | | 1,3-PDO | - | 24 | |
| | | | | | | | | | | | Acetol | - | 12 | |
| | | | | | | | | | | | 2-POH | - | 3 | |
| GA | Double cell | Pt | Pd | RT | - | –1.5 | pH 6 ($NaClO_4$) | - | 33 | - | 1,3-PDO | - | | [13] |
| Glycerol | Double cell | Pt | 80AC/20 CB | 27 | 0.202 | 18.2 | pH 1 ($Na_2SO_4$/ Amberlyst-15) | 8 | - | 84 | 1,2-PDO | 27 | 89 | [19] |
| | | Pt | Pt | 27 | | | | | - | 83.9 | 1,2-PDO | 23 | 90 | |
| Glycerol | Single cell | SS | SS | 70 | 5.21 | - | pH 6.4 | 1.3 | - | 14 | $H_2$ | 0.01 | 5.49 | [22] |

*T – temperature; J – current density; V – voltage applied; t – time; EE – electrochemical (coulombic) efficiency; GC – glycerol conversion; PY – product yield; PS – product selectivity; CBAC – carbon black/ activated carbon composite; CBD – carbon black/diamond composite; 1,2-PDO – 1,2-propanediol; 1,3-PDO – 1,3-propanediol; $H_2$ – hydrogen gas; HDA – hydroxyacetone; GA – glyceraldehyde; Ti/RuO2 – titanium-coated ruthenium oxide; SS – stainless steel; 2-POH – 2-propanol.

## 4. Effect of Reaction Parameters

Electrochemical transformation of alcohols engaged several essential stages-alcohol adsorptions, interatomic bond breakage, electronic charge transfer, the interaction between generated oxygenated species and alcohol fragments within the medium, and desorption of the reaction products **[52]**. The reactivity of these stages plays a major role in the C-C and C-OH breakage bond. Furthermore, the conversion and EE of glycerol are basically determined by (i) the interaction of the glycerol molecules, (ii) the interaction of the adsorbed fragments with the electrocatalyst surface, and (iii) the formation of surface oxides based upon the reaction. In other words, it means that (i) the operating conditions of the ECR process including electrolyte pH, process temperature, current density/applied voltage, etc., and (ii) the geometric and electronic properties of the electrodes all play a significant role in the degree of glycerol conversion and the end-product distribution.

Thus, by altering these reaction parameters, electrochemical performance can be improved by diminishing or slowing the HER reactions, which previously mentioned in Section 2. In general, HER is a multistep process carried out on the surface of a cathode electrode and generating excess gaseous hydrogen (water reduction, Reaction 3). Hence, a synergistic effort between pH electrolyte, electrode potential and electrocatalyst type is needed. This approach has been discussed in many previous publications where HER can be inhibited by: (i) applying electrocatalyst with specific active sites and high HER overpotentials which favours glycerol reduction–carbon-based **[53,54]** and bimetallic catalysts **[55,56]**, (ii) maintaining electrolyte pH by using buffering electrolytes **[57]**, and (iii) lower processing temperature **[58]** which shifts the reaction kinetics towards glycerol ECR. Further discussion of role played by each parameter will be elaborated in their respective subsections. Hence, we could deduce that cross-linking each processing parameter and studying its optimization are very paramount in order to address HER issue as well as enhance its product selectivity, yield and conversion.

### 4.1. Effect of Electrolyte pH

Based upon glycerol ECR results, the pH of the electrolyte plays an important role in controlling oxidation and reduction activities, end-product yield, and selectivity. From previous works of glycerol ECR on Pt electrodes, the nature of the acidic electrolytes – HCl, NaCl/HCl, KCl/HCl, $H_2SO_4$, and $NaHSO_4$- and their resulting pH value showed a major impact on the liquid product yields as well as its EE. Glycerol conversion and PDO yields improved when HCl, strong acidic electrolyte, is utilized compared to other electrolytes. The aforementioned tendency was shown to be correlated with the degree of electrode surface adsorption of the corresponding anions within those electrolytes ($Cl^{-} > SO_4^{2-}$) [49], significantly impacted hydrogen adsorption. Whereas the acidic medium was kept fixed at a pH of 1 as stated in other works [35], exhibits the optimal compromise for oxygenates ECR and HER (pH 1 > 1.3 > 0.7).

According to a recent mechanistic study of the electroreduction of glycerol employing Pt electrocatalysts in an acidic medium [21], this reduction occurred as a result of the interaction of two primary reaction pathways: (a) electrocatalytic hydrogenation, as well as (b) direct electroreduction resulting in the production of acetol. The relationship between the pH of the electrolyte utilized and its overall EE as well as the end-product selectivity of glycerol ECR can both be explained by these findings on the fundamental reaction mechanism of glycerol reduction. According to Hunsom and Saila [21], under the strongly acidic environment of pH 1, a more active oxidation-reduction reaction had been detected via steady-state cyclic voltammetry (CV) curves of the enriched crude glycerol, shown in Figure 3(a). In contrast to neutral and alkaline conditions, it was demonstrated that a variety of peaks (peaks I, II, and III) were formed at pH 1, which was designated as the ideal setting for enhanced glycerol conversion processes. Whereas a neutral medium of pH 7 and a strong basic electrolyte both exhibited almost no sharp oxidation peak within their polarization curves. Although research on the glycerol electro-reduction mechanism route is extremely limited [17,59], this reaction prefers acidic environments to create an acetol intermediate via dehydration, which is crucial for 1,2-PDO production.

Besides that, according to Hunsom and Saila [46], better glycerol conversion to 1,2- and 1,3-PDO was observed under strongly acidic conditions over the Pt surface, were generated by the reduction of acetol and acrolein, respectively, due to the presence of a higher concentration of $H^+$ protons, promotes greater electroreduction/hydrogenolysis reaction. After 13 hours of electrolysis with a constant current density of 0.14 A/cm$^2$, Pt electrocatalyst exhibited its capacity to break the C-C, C-OH, and C-H bonds to form $C_3$ and $C_2$ species. The highest glycerol conversion rate was achieved at pH 1 (100%), pH 11 (62%) followed by pH 7 (46%) [46], shown in Table 2. Due to a larger concentration of $H^+$ and $OH^-$ ions within strong acidic and alkaline media, respectively, which enhance the electrolyte conductivity, the outcomes showed improved conversion rate and better EE (or electrolysis rate) as compared to under a neutral medium [48]. Figures 3(c-f) clearly depicts that acrolein and glycidol are the main reaction by-products produced during the electrolysis under various pH values. While acetol and ethylene glycol were mainly generated under strong basic and acidic conditions as these conditions favored two main reactions-dehydration of adsorbed glycerol (C-H bonds cleavage) as well as C-C bond splitting. The adsorption kinetics of the glycerol electroreduction reaction were examined using the first-order model, and pH studies are fitted using the model. Although it was reported that the greater quantity of products yielded throughout the procedure boosted the glycerol conversion rate, the researchers have not demonstrated the mechanistic pathways of each pH reaction medium on Pt cathode as electrocatalysts.

In a different study by Liang et al. [13] which investigated the effect of the pH of electrolyte over palladium (Pd) electrodes, it is observed that strong acidic condition inhibits the reduction of DHA and GA-primary products of electrooxidation of glycerol-attributed by the absence of hydrogen evolution and hydrogenation/dehydroxylation reactions of those oxygenated compounds as well as other side reactions-isomerization and aldol condensation. At pH 3-8, GA shows higher electroreduction activity with higher selectivity towards the generation of 3-hydroxy propionaldehyde (3-HPA) and further 1,3-PDO, for about 35 and 25%, respectively. Thus, it distinctly shows that the pH of electrolytes with aids from different electrocatalysts allows higher reaction efficiency and greater selectivity towards propanediol and alcohol groups which is in line with observations by Hunsom and Saila [21] as represented in Figure 3(b).

In addition, the pH of electrolytes has been shown to directly impact improving electrocatalyst activity within the electrodes. The organic compound's ionization state, which was discovered to be in either a neutral or protonated form in acid and an anion in an alkaline environment, was revealed to be related to the pH effect [60]. When in an ionic state, it is maintained in the polar solution, restricting the ECR process as well as its adsorption onto the support. Whereas when in a neutral state, it predominantly adsorbed onto the electrode, promoting an ECR reaction to be done. The propensity for adsorption of the organic molecules and protons onto the electrocatalysts usually supported by carbon support and metal-based materials, respectively [35,61].

In conclusion, when performing ECR of glycerol and reduced molecules, it is important to take into account that the electrolyte plays a vital role in determining the condition and availability of the adsorbate species. It also plays a role in determining the reaction pathway that starts the hydrogenation process, which determines the selectivity of the liquid product.

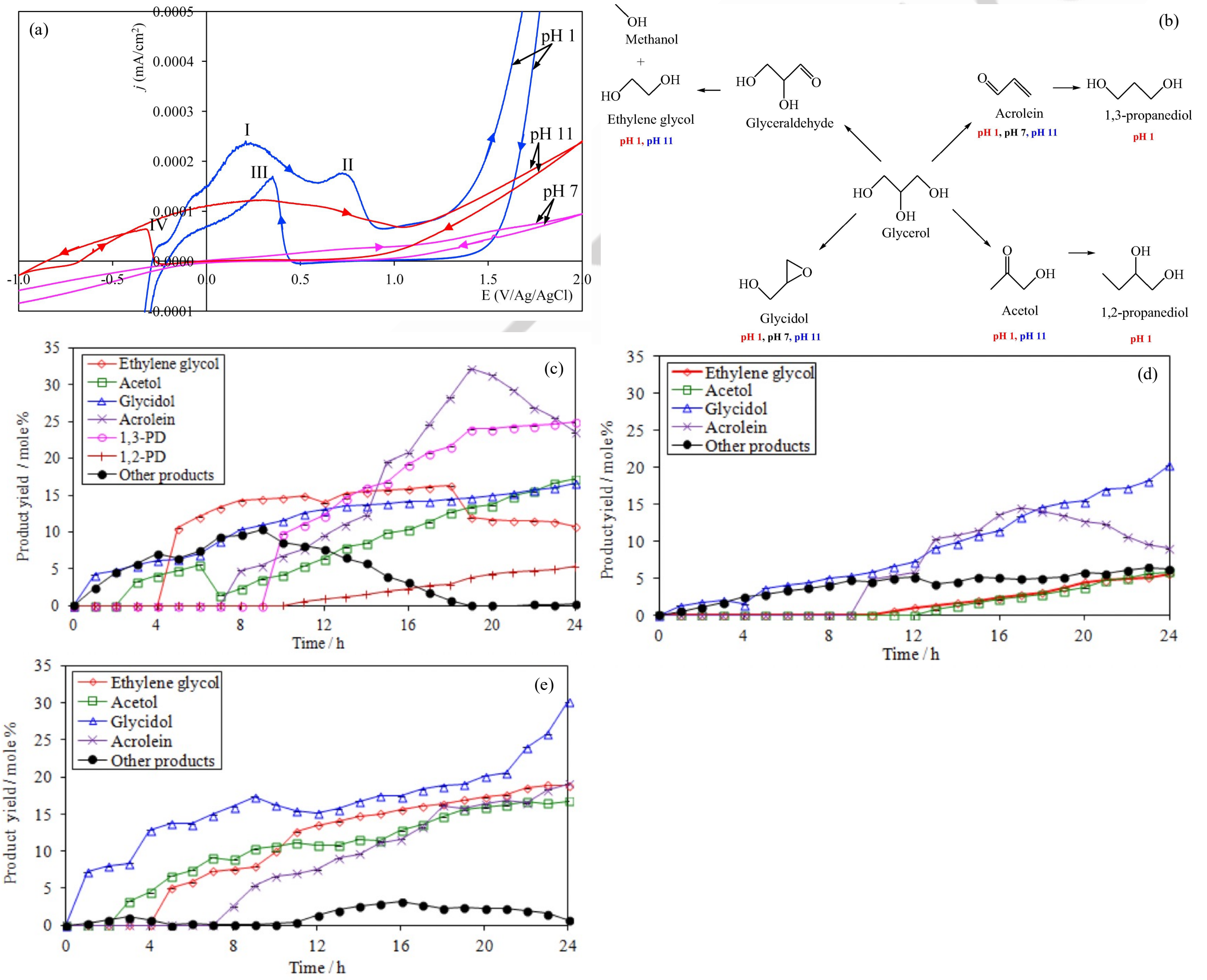


**Figure 3.** (a) CV curve (current density vs applied potential) of enriched crude glycerol at electrolyte pH of 1, 7, and 11 utilizing Pt electrodes. Reproduced from ref. [21] Copyright (2014), with permission from Elsevier. In an anodic scan, peak I (at +0.208 V) presented the oxidation of impurities such as ionic salts while peak II (at +0.712 V) demonstrated the oxidation of glycerol. For the cathodic scan of pH 1, one oxidation peak (peak III) of the incomplete oxidation of carbonaceous residues over the Pt surfaces was observed at +0.351 V, hindering the reduction peak detected around +0.5 V. (b) Summary of the possible pathway for glycerol electroreduction and oxidation within diverse pH of electrolyte. Reproduced from ref. [5] Copyright (2019) with permission from Elsevier. Liquid by-product distribution of glycerol ECR over a Pt electrode with the applied current of 4.5 A at different initial electrolyte pH of (c) pH 1, (d) pH 7, and (e) pH 11. Extracted from ref. [46] Copyright (2014), with permission from Elsevier.

### 4.2. Effect of Reaction Temperature

Glycerol ECR is an endothermic reaction that requires an electricity supply and a specific amount of heat to catalyze the reaction. Thus, this mechanism indicates that EE, conversion rate, and liquid product selectivity of ECR are greatly impacted by a certain higher range of temperature (30-80 °C) compared to lower glycerol conversion at ambient temperature. Significantly, reaction temperature has been shown to directly plays a critical role in increasing the electroreduction kinetics and accelerating the C-C and C-O bond breakage during the reduction of oxygenated compounds [59].

Increases in operation temperature resulted in additional hydrogenation of the organic molecules when the ECR of glycerol was taken into account, performing a significant impact on glycerol conversion rate and end-product yields [19,22,62]. For instance, based on works by Lee et al. [62], within the operating temperature range of 25-80 °C, over a Pt catalyst surface, the conversion rate increased gradually from 0.406-0.774 $h^{-1}$, respectively, indicating the glycerol electrochemical conversion is thermally activated. Rahim et al. [63] have evaluated the impact of high process temperature (above 100 °C), which hindered the glycerol conversion due to several factors of vaporization of by-products with a lower boiling point, and quicker reduction of $H^+$ ions into $H_2$ (see Figure 4). In another work of electrochemical reduction of model compound furfural into furfuryl alcohol, done by Chen et al. [64], using Pt supported on activated carbon fiber (ACF) has shown the impact of temperature within the overall electrochemical reaction. Between 30-50 °C, the EE improved gradually, 78-85%, while it declined to 74% at 90 °C due to additional heating which leads to a side reaction of electro-dimerization. The elevations in reaction temperature to over 80 °C often favor HER and cause a decline in overall electrochemical ECR efficiency. This event happened, under high processing temperatures, the increased rates for $H_2O$ oxidation at the anode led to a significantly high flux of $H^+$ species to the cathode, favoring HER to occur. Moderate operating temperatures should be employed also to reduce the incidence of reactor plugging and catalyst deactivation due to the aging process [65]. Aging occurs during storage as a result of secondary reactions, in which condensation and polymerization reactions increase the viscosity of the bio-oil and cause solid formation [66].

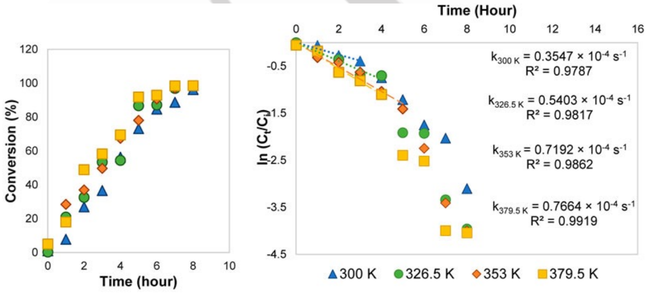


**Figure 4.** Glycerol conversion via ECR and its first-order kinetic models at different processing temperature – (Δ) 25, (○) 50, 80, and 100 °C. Reproduced from ref. [63] Copyright (2022), with permission from Frontiers.

On the other hand, it is best to discuss the incorporation of the electrocatalysts with the elevated temperature here. They are employed to remove oxygen from the oxygenated organic substance via the improved exophilicity nature of their active sites. The selection of electrocatalysts is very crucial in investigations of operating temperature as an excessive amount of heat can render thermally unstable catalysts inactive. Currently, in order to evaluate how temperature affects the reaction rate, experimental works of glycerol ECR over electrocatalysts at different temperatures using the Arrhenius equation ($K = A.e^{-Ea/RT}$) could be done. However, intrinsic temperature (T) is not directly proportional to the activation energies ($E_a$) of the electrocatalysts. This relationship between T and $E_a$ is also demonstrated by the equation. This equation shows that as T increases or $E_a$ decreases (as electrocatalysts are equipped), the rate constant (K) will be increased which is directly proportional to the rate of the chemical reaction and hence, making it useful for calculating the rate law parameters. Yet, from authors' knowledge, there is still wide knowledge gap that exist related to the synergistic effect between the operating temperature with the nature of electrocatalysts (its $E_a$ and structural changes) [50,51], within glycerol ECR.

### 4.3. Effect of Electrode Potential and Current Density

In general, electrochemical conversion can be performed either by controlling the current density–galvanostatic-or the applied potential potentiostatic, where both variables show significant impact on the EE and product selectivity in reduction of biomass-derived feedstocks even at ambient temperature and mild pressure. Fundamentally, by altering the applied potential and current, the desired molecular conversions can be successfully predicted. From a previous study [47], glycerol conversion using Pt electrodes was insignificant at open circuit potential of absence electricity, whereas, an improved redox reaction performance was observed when electric potential or current was applied.

In galvanostatic electrolysis, Rahim et al. [63] as well as Hunsom and Saila [21] have discovered that glycerol conversion increased along with the increasing current density applied, which obeyed Faraday's second law of electrolysis [67]. In short, the law states the amount of substance produced at each electrode-conversion rate of glycerol is directly proportional to the quantity of charge flowing through the cell. Glycerol conversion, by engaging a first order kinetic model, which is represented by the rate constant of the reaction showed an increasing trend of 0.00074, 0.0011, 0.0016, and 0.0045 $min^{-1}$ at 0.08, 0.14, 0.24 and 0.27 $A/cm^2$, respectively, as shown in Figure 5. At the onset of their studies [21], an interesting observation gathered is that acrolein and 1,3-PDO were only produced at current densities between 0.14 and 0.24 $A/cm^2$, which shows that dehydration of the adsorbed glycerol molecule at the second hydroxyl group is not favored at values below 0.08 $A/cm^2$ and over 0.27 $A/cm^2$. This trend is also in line with the study by Rahim et al. [63]. Moreover, a high current can speed up the electrolysis process by enabling the conversion of glycerol to 1,2- and 1,3-PDO. Thus, based on the selectivity results, a reaction pathway was postulated for the ECR of glycerol, where at a specific optimized applied current, selective production of PDOs is favored. However, overly high current density can negatively impact the glycerol conversion due to the presence of other parasitic side reactions of glycerol decomposition to gaseous compounds [68]. Next, it will also lead to further electrode corrosion via dissolution, gasification, or exfoliation where these mainly happened by carbon-based electrodes in an acidic medium.

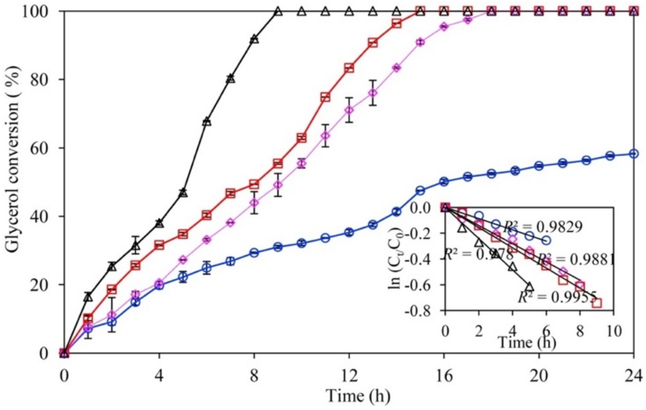


**Figure 5.** Glycerol ECR conversion over a Pt grid electrode under a strong acidic condition (at pH 1) with a variety of applied current densities – (○) 0.08, (◊) 0.14, (□) 0.24, and (Δ) 0.27 A/cm$^2$. Reprinted with permission [21] Copyright (2014), with permission from Elsevier.

On the other hand, within the potentiostatic mode, Liang et al. [13] reported that applied voltage during ECR of oxygenated compounds affected the EE, product selectivity, and conversion rate of the electrolytes. In the electroreduction conversion of GA, 25% of the highest 1,3-PDO selectivity had been recorded at -1.1 V versus RHE within the LSV scan at different potentials of -0.7 to -1.7 V vs RHE. While Yildiz et al. [69] studied that the formation of $H_2$ gas at the cathode via glycerol electrochemical conversion was heavily favored at higher applied potential (2V>1V) under similar conditions. Similar results have been obtained for the electrooxidation of glycerol, where electrode polarization has been demonstrated to affect product selectivity [30,70]. Dai et al. [30] reported that glycerol has been oxidized into lactic acid (LA) on Au10-Pt90 surfaces at low potentials with significant selectivity of about 70%. It was proposed that low electrode polarization promoted the synthesis of LA (base-catalyzed dehydration succeeded by Cannizzaro rearrangement) at Au-Pt surfaces while impeding the metal-catalyzed oxidative activation and subsequent oxidation of the derivatives.

Hence, the fact that the reaction occurs in benign circumstances, without the presence of any poisonous or highly reactive reactants, suggests that the application of applied potential or current regulation was successful in controlling the distribution of the reaction's products and its mechanism paths. Plus, an optimized amount of potential or current applied can majorly aid in generating intended by-products within the ECR reaction.

### 4.4. Effect of Electrocatalyst

Electrocatalyst is one of the main components of an electrochemical reduction reactor system which is utilized to speed up the electrochemical reactions that occur at the electrode surfaces or on solid/liquid interfaces. The interactions between the adsorbed species and the electrode surface primarily depend on the nature of the electrocatalyst employed. A good electrocatalyst should exhibit a large surface area for electrocatalytic dispersion, higher number of active sites, strong chemical stability under different electrolytes, and excellent electrical conductivity [71]. The alteration of catalyst nature, thus, can control the electroreduction activity by permitting adsorption and desorption on its surface, plus, offers acceleration of mass transfer between different active sites during the catalytic reaction [72].

In the case of glycerol ECR, Pt electrode is the most favored electrocatalyst as its working electrode due to its excellent electrochemical activity toward redox reactions–high conversion rate in shorter electrolysis time [21,73]. Hence, at the cathode, it is acknowledged that glycerol molecules are reduced to other by-products contributed by synergistic effect from the catalyst and the presence of electricity, as illustrated in Figure 6. Namely, there are few tactics on how alcohols (i.e., glycerol) converted electrochemically over an electrocatalyst surface: alcohol adsorption, inter-atomic bond breakage, reaction between the oxygenated species (generated at anode) and the fragments from the alcohol, desorption of the reaction products and the electronic charge transfer [52]. Figure 6 illustrated several alcohol adsorption pathways which includes the primary or/and secondary C–Pt bonds over the heterogenous electrocatalyst during the reaction. Each pathway will then manipulate the formation of different valuable end-products. In the mechanism shown in Figure 8, glycerol is reduced to 1,2- or 1,3-PDOs in a subsequent two-electron transfer step. While 1- or 2-POHs are formed either by the next two-electron transfer step of PDOs over catalyst surface or via secondary alcohol reduction. Based on literature, these possible reduction and oxidation reaction pathways on electrocatalyst were mostly studied using the density functional theory (DFT) calculations [12,73]. As mentioned by Cui et al. [12], the adsorption of primary or/and secondary C is favors by its calculated adsorption free energy.

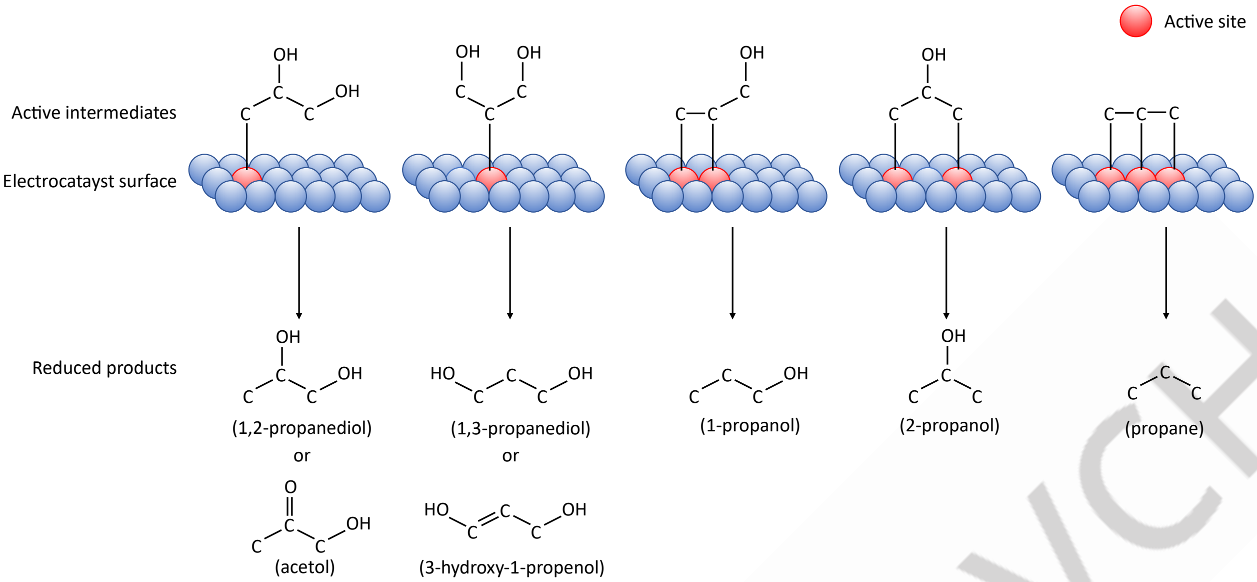
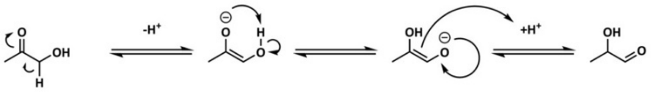


**Figure 6.** Possible reaction pathways of the electrocatalytic reduction of aqueous glycerol.

From previous works, it is demonstrated that Pt electrode is robust, highly stable, and almost flexible to be used in various reaction conditions of different pH of electrolyte, as well as extremely employed operating temperature and current/applied potential [5,46]. However, the high price of Pt materials is one of its practical problems. Thus, there are increasing number of studies toward non-Pt electrocatalysts that have been done in these coming years where Au, Pd, and non-noble metal-based electrocatalysts show promising potential as substitutes for glycerol ECR [18,19,49,62]. In the literature, Rh- or Pt-based catalysts combined with W-based co-catalyst or modifier are relatively effective in the glycerol hydrogenolysis to 1,3-PDO [74].

Sauter et al. [49] investigated the contribution of various non-noble metals in an acidic medium toward the electrochemical deoxygenation of glycerol derivatives, HDA or acetol. According to their study, it is stated that Fe and Al were superior, in terms of 1,2-PDO selectivity, compared to other non-noble mono-metallic electrocatalysts as the working electrode (see Figure 7). The performance comparison is as follows: Al=Fe>Mo>Cu>Ni>>Ti>>Zn>>Pb. Whereas, in the case of the ECR reaction rate of HDA into PDOs, the Fe electrode exhibits better EE and a higher reaction rate of 780 mmolh$^{-1}$m$^{-2}$ due to its exophilicity nature which allows a higher reduction rate as compared with others–Fe>Cu>Mo>Al>>Ni). The outcome of their study is in line with the fact that Fe is a good reducing agent-proven by its significant reduction rate and abovementioned reduction product selectivity. Based on Scheme 2, acetone and 1,2-PDO were able to be generated thru direct ECR of HDA. Sauter et al. [49] observed that the hydroxyl group in HDA is always preferred to be reduced into ketone group (acetone) [75], instead of 1-POH. However, small number of 1-POH was detected to be generated contributed by the Lobry de Bruyn-Alberda van Ekenstein transformation (LdB-AvE) of acetol to 2-hydroxypropanal, as shown in Scheme 3 [76], which then reduced to 1-POH.



**Scheme 3.** Reaction mechanism of the Lobry de Bruyn-Alberda van Ekenstein transformation. Extracted from ref. [49] Copyright (2023), with permission from Wiley-VCH.

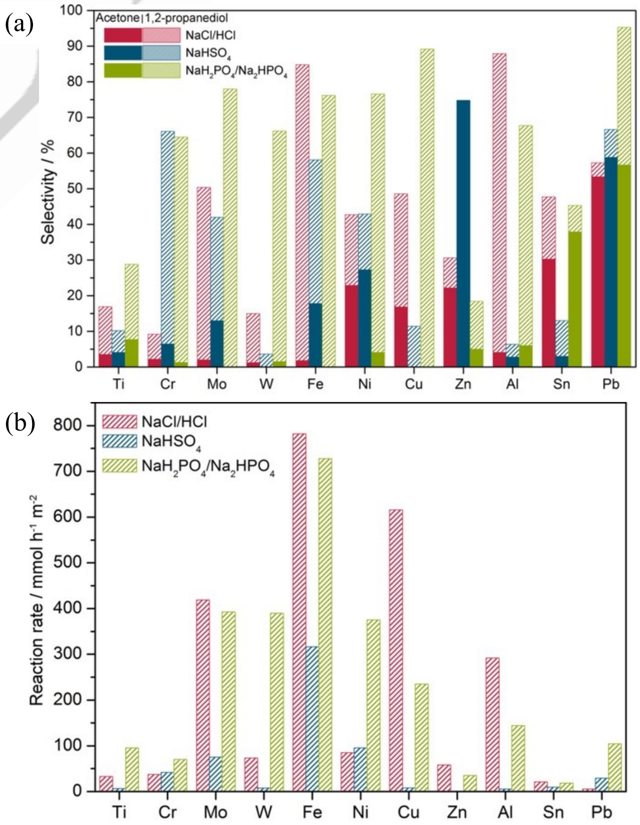
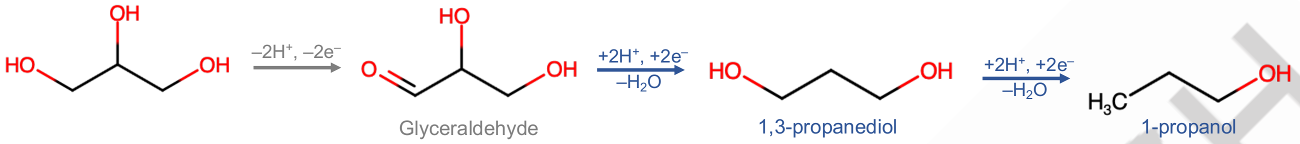


**Figure 7.** ECR of HDA under the application of different non-noble metals as electrocatalysts on the composition of the electrolyte solution. (a) Acetone and 1,2-PDO formation selectivity and (b) ECR reaction rate of formation of 1,2-PDO from HDA as a function of electrode materials and electrolyte solution. With a

constant working electrode voltage of 1.8 V (vs. Ag/AgCl), all reactions were carried out in a partitioned H-type cell at ambient temperature. Reproduced from ref. [49] Copyright (2023), with permission from Wiley-VCH.

In a different work by James and co-workers [18], Pb and Zn, non-noble active metals, have excellent features as active metal electrodes for Clemmensen reduction which favors the cathodic reduction of glyceraldehyde (GA) to 1,3-PDOs. The Clemmensen reduction of carbonyl groups used to reduce carbonyl groups in aldehyde or ketone to methylene bridge within hydrochloric acid medium. In this study, as shown in Scheme 4, glycerol was first oxidized into anodic GA in chloride media. Next, the high GA selectivity sufficiently feed the coupled cathodic dehydroxylation to 1,3-PDO. However, compared with the other studies, this approach seems to have a minor impact on glycerol ECR due to its lower conversion rate and product selectivity.



**Scheme 4.** Reaction pathways of tandem glycerol oxidation and cathodic reduction (Clemmensen reduction) over Pb and Zn electrocatalyst.

Recently, the utilization of carbon-based catalysts has shown promising potential due to its comparable EE, and excellent reactivity rate with Pt-based electrocatalysts. Rahim et al. [19] and Lee et al. [62] utilized carbon-based electrodes directly for glycerol electroreduction studies. The practicability of carbon-based materials–graphene, and carbon nanotubes (CNT) are limited due to their high price and complicated synthesis process using hazardous and specific reagents [77–80]. Conversely, graphite, activated carbon (AC), and carbon black (BC) are very cheap as well as possessing surface morphology and chemistry that are easily tuned depending on the desired application via surface functionalization/doping with various functional groups-polymer [81,82], metals [83–85] and heteroatoms [86,87].

Rahim et al. [19] studied glycerol ECR by using AC reinforced with BC and redox mediator of Amberlyst-15 was also used, to improve the electron transport between the electrode and substrate during the reaction. From this work, approximately 90% of 1,2-PDO selectivity has been recorded, same performance as Pt cathode. They also discovered that high AC content enhanced the electroactive surface area of the electrode and favored the acetol-to-1,2-PDO generation via the C–O bond breakage. In a different study, Yan et al. [87] introduced nitrogen over the surface of AC materials via a doping approach, thus, leading to defect formation on the surface of the electrode. Throughout this study, a defective AC electrode which is highly porous with a high number of active sites has demonstrated excellent HER-suitable for reduction reaction, especially in acidic conditions. It serves as a support matrix to promote the dispersion of the active components and allows feedstock molecules and electrolytes to enter the active sites [88], which ultimately boosts the electrocatalytic activity.

Insights on the glycerol ECR across a variety of noble and non-noble metals, as well as carbon-supported surfaces, indicated that the performance of hydrogenolysis and conversion rates were significantly influenced by the strength of hydrogen bonding to the electrode surface. Conclusively, metal-based materials will improve the adsorption of protonated glycerol molecules while carbon support favors the adsorption of excess organic molecules. Thus, this approach will optimize the ECR reaction. Plus, non-optimal HER catalyst metals encouraged higher ECR rates, while optimal HER catalyst metals resulted in lower rates and EE of the conversion.

## 5. Conclusion and Outlook

Electrochemical valorizations of biomass-derived resources like glycerol demonstrate a feasible alternative to the conventionally applied thermochemical procedures in large-scale industry. Plus, the successful electrochemical pathway can further be amplified in its application for upgrading other complex oxygenated compounds-bio-oil, wastewater, and waste oil-due to the fact that this route exhibits a significant balance between end-product selectivity and milder operational environments, with facile processing methods and low demand for intricate downstream purification. Therefore, with more investigations, electrochemical valorization can provide paramount contributions in terms of reaction efficiency, product selectivity as well as operational flexibility.

According to the thorough literature review above, electrochemical upgrading of glycerol was dominated through an electrooxidation strategy, and thus, glycerol ECR is rather still scarce. Furthermore, most published works to date have taken an experimental approach of proving the influence of each major process parameters-pH electrolyte, current density/voltage applied, process temperature and electrocatalyst nature-towards EE, reduction reaction rate, catalytic activity, and product selectivity. It is found that the synergistic effects of the operating parameters result to optimized glycerol ECR performance. Nevertheless, the generation and control of $H^+$ protons within the medium, as well as its interaction with adsorbed glycerol species (via oxidation and reduction process), are the crucial points in engineering the electrochemical efficiency and selectivity. In the case of glycerol ECR, higher current density/voltage applied under strong acidic conditions demonstrated efficient electroreduction and hydrogenolysis reaction. Plus, these conditions also favor the selective ECR with higher production of reduction-derived compounds-acetol, acetone, PDOs, and POHs. Other than that, the impact of electrocatalysts on the improvement of product selectivity and reaction rate has been consistently reported in current studies where it is mentioned that Pt-free and non-noble metallic electrocatalysts have demonstrated promising performance thus reducing the Pt-based catalyst dependency. The use of these types of electrocatalysts has yet to show its potential for industrial-scale application, showing that there is still a knowledge gap in discovering novel electrocatalyst materials.

Here, we also summarized various possible reaction pathways of ECR and electrooxidation of glycerol feedstocks into high value-added compounds over electrocatalyst surface within simple electrochemical cells, which is hardly found in other published review papers. The mapping of all potential reaction routes implicated in the routes is crucial in order to recognize the reaction products or intermediates formed, emphasizing the fundamental understanding of reaction pathways and specifying the electrocatalyst contribution towards glycerol deoxygenation and reduction. However, an in-depth further study regarding electrocatalyst selection is still needed on this topic to provide a better understanding of the mechanism.

Furthermore, based on the findings from this review, several critical outlooks for future research are as follows:

1. There is lack of deep investigations on the influence of operating temperature within the glycerol ECR reported by previous works. It serves as a knowledge gap in improving the electrocatalytic activity and selectivity. Based on electrolysis and catalysis theory, elevated temperature can increase the rate of reaction by increasing the kinetic energy of the molecules more than their activation energy, allowing them to break their bonds. Thus, further study regarding this topic could lead to new and improved electrocatalysts and reaction conditions for a variety of chemical processes.
2. The recurring issue related to the occurrence of parasitic side reactions, which includes HER and catalyst poisoning, during the electrolysis also need to be addressed. This approach is possible to improve product yield and selectivity of electrolysis. There are number of further directions that can be achieved from here – other than developing new catalysts and optimizing electrolysis conditions, utilizing new electrolytes is another important factor affect the reaction efficiency. This is due to the fact that different electrolytes have different properties where aqueous solution as well as strong acids and bases are more prone to parasitic side reaction than organic solvents [89,90]. Furthermore, the employment of membranes is possible to address this issue by separating the anode and cathode compartments of an electrolyte.

   In addition to the above, research on the valorization of by-products from side reactions into higher value-added products should be prioritized. By valorizing these by-products, it would be possible to improve its economic viability and to reduce the environmental impact of electrolysis in the future.
3. The development of a basic understanding of selective glycerol ECR over Pt-free electrocatalysts is still subpar, despite the several recent publications of different parameter optimization research, which stated in this review. The absence of controlled operating conditions and the electrocatalysts' ambiguous nature when reacting within these parameters constitute the reasons for the majority of inconsistencies in the reported data. To solve this issue, systematic investigations with the implementation of machine learning (ML) prediction models are essential. Artificial intelligence (AI) and ML will most likely hasten the selection of electrocatalyst combinations along with the optimization of operational parameters [91,92]. Besides, prediction towards the best possible electrocatalysts also can be done using several common input features (descriptors) of the catalysts – its bulk Wigner-Seitz radius, atomic number, atomic mass, electronegativity, ionization energy, density at RT, fusion enthalpy, surface area and its pore diameter [93,94].

   The use of AI and ML in glycerol ECR is still in its early stages, but it has the potential to effectively construct electrochemical systems for high EE, activity, and particular product selectivity with specified electrocatalyst and reaction conditions. Thus, this could lead to the development of new and more sustainable pathways to produce biofuels, chemicals, and other by-products from glycerol.
4. Paired electrolysis (or also called co-electrolysis) with electrocatalytic oxidation and reduction reactions is gaining many interests nowadays, as it offers number of synergistic benefits. As this approach applied in a reactor with two separate compartments connected by a selective ion exchange membrane, it enables the simultaneous conversion of glycerol at the cathode and the oxidation of reactants at the anode, facilitating the integration of multiple electrochemical processes into a single setup. This reduces the need for separate reaction systems, leading to improved resource utilization and process efficiency. Secondly, the ECO reaction at the anode can help maintain the electrochemical balance by consuming electrons and protons produced during the ECR process, enhancing the overall efficiency of the system.

   There are several recent publications that agree with these ideas. Some of them studied paired electrolysis of glycerol with $CO_2$ [95,96] and highlighted that this approach also useful in enhancing their economic viability by reducing the process's operating costs and carbon footprint. As a result, new pathways towards a carbon-neutral cradle-to-gate process can be discovered.

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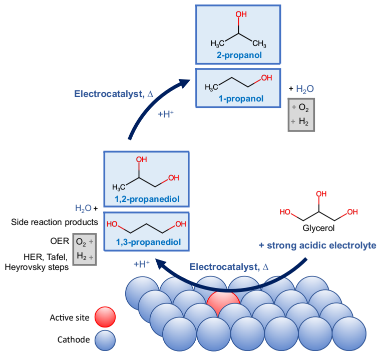

Electrocatalytic reduction (ECR) of glycerol: ECR is a promising technology to produce biofuels from a renewable resource of glycerol. The reaction was carried out using electrocatalysts under milder condition, and the products can be tailored to meet specific needs. However, there are still challenges that need to be addressed to make glycerol ECR a more viable technology – lowering catalyst costs, improving product yields and selectivity.