

Product Distribution of Electrochemical Conversion of Glycerol via Pt Electrode: Effect of Initial pH

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The effect of the initial solution pH (1, 7 and 11) on the glycerol conversion and product distribution by electrochemical technique with a Pt electrode was explored at a laboratory scale and ambient condition. Under steady-state cyclic voltammetry (CV), the electrochemical conversion of glycerol to various reaction intermediates and products was observed. Under a galvanostatic mode, the glycerol conversion level as well as the product distribution and yields were highly dependent on the initial electrolyte pH. The conversion of glycerol underwent first-order rate kinetics model with a rate constant of 2.95×10^{-3} , 7.95×10^{-4} and $9.20 \times 10^{-4} \text{ min}^{-1}$ for an initial electrolyte solution pH of 1, 7 and 11, respectively. 1,2-Propanediol (1,2-PD) and 1,3-PD were only generated at pH 1, while ethylene glycerol, acetol, glycidol and acrolein were formed in the electrolytes at all three tested pH values. Product analysis revealed that the electrochemical conversion under these conditions could convert glycerol directly and quickly to glycidol, but more slowly to ethylene glycerol, acetol, acrolein, 1,2-PD and 1,3-PD.

Keywords: Glycerol; Electrosynthesis; Pt electrode; Cyclic voltammetry

1. INTRODUCTION

Glycerol is the main by-product from biodiesel production, with approximately 100 kg of glycerol being generated per ton of biodiesel produced (10% (w w⁻¹)) [1-2]. The growing biodiesel market has generated an oversupply of glycerol, resulting in a decreased commercial price of glycerol that negatively impacts upon the economy of biodiesel production. Thus, the current exploitation of glycerol as a raw material focuses on the transformation of glycerol to added-value products because its molecule is rich in functionalities with three -OH groups [3]. A diverse array of processes to

transform glycerol into more valuable chemicals have been developed, such as pyrolysis [4-7], gasification [8-10], selective oxidation [11, 12], biological processes [13-15], esterification and acetylation [16, 17], and hydrogenolysis [18-22]. However, many of these processes have drawbacks, such as a lack of sufficient selectivity and yield. Some processes require specialized or high running-cost production systems (e.g., high temperature and pressure) or require a long reaction time, preventing them from being commercially viable [23]. To address these drawbacks and to facilitate the commercial conversion of glycerol to valuable compounds, electrochemical conversion approaches have been evaluated as an alternative method that could be used to convert glycerol waste from the biodiesel industry to valuable alternative compounds. This is because of its relative simplicity and robustness in structure and operation.

In general, the electrochemical conversion of alcohols involves various different steps: alcohol adsorption, breaking of the inter-atomic bonds, electronic charge transfer, reaction between the oxygenated species and fragments from the alcohol, and desorption of the reaction products [24]. As a result, the conversion efficiency depends on the: (i) interaction between the catalyst surface and the alcohol molecules, (ii) interaction between the catalyst surface and the resulting adsorbed fragments from the original alcohol molecules, and (iii) formation of surface oxides. In other words, the degree of glycerol conversion, the product distribution obtained and the reaction mechanism depends significantly on (i) the geometric and electronic properties of the electrodes, (ii) the glycerol concentration, and (iii) the working conditions of the electrochemical conversion process (electrolyte solution, solution pH, temperature, etc) [23].

During controlled potential electrolysis, glycerol can be oxidized to formic acid, oxalic acid and glycolic acid in an acid electrolyte (0.1 M HClO₄) when the potential of electrolysis was set in the so called "oxygen region". However, the selectivity towards the formation of glyceraldehyde is very high when the applied potential is chosen before the beginning of the oxidation of the electrode surface. Conversely, in an alkaline electrolyte (0.1 M NaOH), very few dissociation products were detected [25]. A simple application of a low voltage (1.1 V vs. Ag|AgCl) to a solution of glycerol (50 mM) buffered at pH 9.1 with bicarbonate (0.2 M) in the presence of catalytic TEMPO (7.5 mM) could oxidize glycerol selectively to 1,3-dihydroxyacetone (DHA) over a glassy carbon electrode [26]. However, prolonging the reaction time resulted in the formation of hydroxypyruvic acid.

By using CV, glycerol was first oxidized in alkaline media (0.1 M NaOH), to glyceric acid on both gold (Au) and platinum (Pt) electrodes with a lower overpotential on Pt electrodes. Afterwards, glyceric acid was further oxidized by cleavage of a C-C bond into glycolic acid and formic acid on both electrodes [27]. However, a much higher conversion activity of glyceric acid to glycolic acid and formic acid was observed on a Au electrode than on a Pt one, which was ascribed to the higher surface oxidation potential of Au compared to Pt. In a strong acid electrolyte (pH 1, H₂SO₄), glycerol was converted to various added-value products, such as 1,2-propanediol (1,2-PD), 1,3-PD, glycidol, etc [28]. The presence of bismuth (Bi) on the Pt/C electrode in 0.5 M H₂SO₄ can block the oxidation of the 1°-OH group of glycerol, resulting in the oxidation of the 2°-OH group to provide 100% selectivity in the synthesis of DHA [29]. The templated binary Pt₈₄Ru₁₆, Pt₉₆Sn₄ and ternary Pt₈₈Ru₆Sn₆ catalysts supported on a glassy carbon electrode enhanced the complete oxidation of glycerol to CO₂ in 1.0 M KOH [30]. The electrooxidation of glycerol on a palladium-rhodium (PdRh) electrode in alkaline

media (0.1 M KOH) yielded carbonate (CO_3^{2-}) as the main product and glyceraldehyde, glycerate, glycolate and oxalate as minor products [31]. For application to power generation, approximately $10 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-3}$ (reactor volume basis) of H_2 was produced from glycerol over Pt on a ruthenium-iridium (RuIr) oxide catalyst in a proton exchange membrane (PEM) electrolysis cell with an energy efficiency of 44% [32]. Although this production rate is high compared to that obtained with microbial cells, it is still low compared with a conventional PEM water electrolysis cell. In the gas phase at an intermediate temperature (235–260 °C), C1 (CO_2 , CO, CH_4), and C2 (C_2H_6 and glycolic acid) compounds plus H_2 were the main reaction products formed from the electro-oxidation of glycerol with a Pt/C electrode. The selectivity for the C1 products (CO_2 , CO and CH_4) increased with increasing electrode potential [33].

In this work, the galvanostatic mode of electrochemical conversion was used to convert glycerol in electrolyte solutions of three different pH values (pH 1, 7 and 11). The types of generated products as well as their yields were traced. Finally, the mechanism of the electrochemical conversion of glycerol was proposed.

2. EXPERIMENTAL

The aqueous glycerol solution was prepared from a commercial glycerol stock (99.5%, Fisher) at a constant initial concentration of 0.3 M. The pH of the glycerol solution was adjusted by analytical grade H_2SO_4 (98%, Qrec) or NaOH (1 M, Qrec) as required. The electrochemical conversion of glycerol was performed at a constant CV using a Potentiostat/Galvanostat (Auto Lab, model PG stato). Two cylindrical Pt grids with a surface area of 31.82 and 121.38 cm^2 were used as the working and counter electrodes, respectively, while $\text{Ag}|\text{AgCl}$ was used as the reference electrode. The scan potential was varied in the range from +2.0 to -0.5 V at a scan rate of 5 mV s^{-1} , and the system was agitated by a magnetic stirrer at a constant rate of 650 rpm. The product composition after electrolysis at steady-state CV was examined by gas chromatography-mass spectrometry (GC-MS, G3174A, Agilent) equipped with a flame ionization detector.

The electrochemical conversion of glycerol under galvanostatic mode was explored at a laboratory scale at ambient temperature (~ 25 °C) and pressure (~ 101 kPa). The electrochemical reactor was made from Pyrex glass having a total capacity of 600 mL. The temperature of electrolytic cell was controlled by a cooling system. A regulated DC power supply (ZS 3205-2X type) was employed to supply the external electricity at a galvanostatic mode (0.14 A cm^{-2}). The conversion of glycerol (calculated from Eq. (1)) as well as the yield of value-added products (calculated from Eq. (2)) were analysed by high performance liquid chromatography (HPLC: Agilent 1100) with a RID-10A refractive index detector. The stationary phase was a Pinnacle II C18 column (240×4.6 mm) and the mobile phase was a 99.9:0.1 (v v^{-1}) ratio of 10 mM H_2SO_4 : pure CH_3OH , passed through the column at 0.5 mL min^{-1} .

$$\text{Glycerol conversion (\%)} = \frac{\text{amount of glycerol converted (C-based mole)}}{\text{total amount of glycerol in reactant (C-based mole)}} \times 100 \quad (1)$$

$$\text{Yield (\%)} = \frac{\text{amount of glycerol converted to each product (C - based mole)}}{\text{total amount of glycerol in reactant (C - based mole)}} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Steady-state CVs of glycerol solution and supporting electrolytes

The typical steady-state CVs of a 0.3 M glycerol solution and supporting electrolytes at different initial pH values (1, 7 and 11) with an applied potential of +2.0 to -0.5 V are shown in Fig. 1. In a strongly acidic (pH 1) electrolyte solution in the absence of glycerol (Fig. 1a), the utilized Pt electrode showed a quasi-reversible system at the anodic and cathodic scan regions. A small increase in the current was observed at too high a positive ($E > +1.3$ V) or too low a potential ($E < -0.25$ V), which is related to the oxidation of H_2O to O_2 (region I) and the reduction of H^+ to H_2 (region II), respectively. In the presence of glycerol, various anodic current peaks were observed in the anodic and cathodic scan regions. The first oxidation peak (peak A), observed at 0.55 V, in the anodic scan corresponds to the oxidation of glycerol (1.8 mA). At a potential greater than +0.75 V, a sharp increase in the current compared with the blank current was observed. The shoulder peak (peak B) connected to the oxygen region (region I) was also attributed to the oxidation of glycerol. During the cathodic scan region, after the reductive peak of Pt-oxide (peak C), one sharp peak (peak D) was observed that was attributed to the incomplete oxidization of carbonaceous residues on the catalyst surface during the negative sweep [34-35]. These carbonaceous residues can accumulate tightly on the Pt surface, blocking the active catalyst sites for subsequent reactions and so resulting in sluggish anodic reactions [35].

In a neutral (pH 7) electrolyte (Fig. 1b), a very low current was detected in the CV plot in the presence of the supporting electrolyte without glycerol except for in the regions in which the O_2 (region I) and H_2 (region II) were generated. The presence of glycerol led to a slightly higher current over the investigated potential range. Nevertheless, no sharp peak was observed, suggesting the accumulation of strongly absorbed hydroxyls on the electrode surface under the neutral condition. In a strong basic (pH 11) electrolyte (Fig. 1c), a very low current was detected in the presence of the supporting electrolyte only, except again for in the regions I and II. In the presence of glycerol, two broad oxidation peaks were observed at a peak potential of -0.03 V (peak A) and +0.32 V (peak B) in the forward scan. Interestingly, both peaks were shifted to a more negative potential compared with those at pH 1, indicating that the oxidation of glycerol occurs more easily at pH 11 than at pH 1 (Fig. 1a). For the backward scan, no oxidation was observed, suggesting that the electrode is not poisoned in the basic medium. Typically, the poisoning effect on the electrode depends significantly on the type and concentration of the supporting electrolyte as well as the type of electrode. The use of 1.0 M NaOH as a supporting electrolyte for glycerol oxidation can enhance the formation of a small poisoning effect on the Pt electrode surface [25], which can limit the glycerol adsorption rate on the freshly reduced Pt surface during the relatively rapid negative potential sweep. The oxidation of

glycerol on a PdRh electrode in 0.1 M KOH resulted in the production of CO_3^{2-} as the principal product [31].

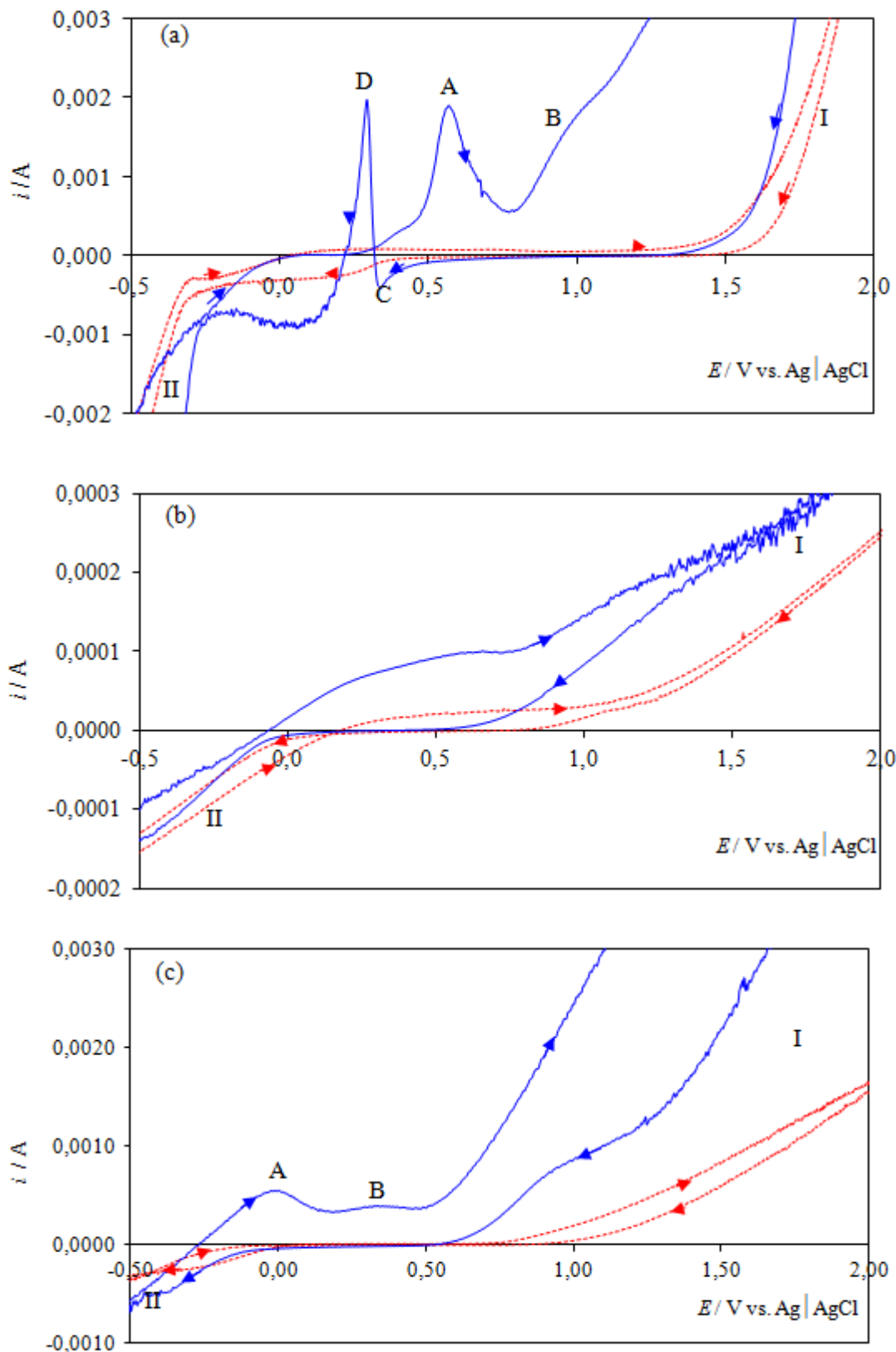


Figure 1. Polarization curve of 0.3 M glycerol at (a) pH 1, (b) pH 7 and (c) pH 11 over Pt electrode.

The product compositions following the glycerol electrolysis by CV were traced by GC-MS analysis. The presence of lower and higher molecular weight products than glycerol were observed to vary as a function of the initial electrolyte pH (data not shown). The identities of compounds determined through matching their mass spectra in the GC-MS computer library were deemed to be reliable and are summarized in Table 1. Acetol, glycidol and 2-methyl-2-pentanol were generated by the electrochemical conversion of glycerol at all three investigated electrolyte pH values. Other compounds, such as 1,2-PD, 1,3-PD, 1,2-butanediol and 5-methyl-1-heptanol, were only produced at pH 1, whilst acrolein and glyceraldehyde were only produced at pH 7, and 2-hexanol, 2,4-dimethyl-1,3-dioxane and 4-methyl-1-hexanol were only found at pH 11.

Some of these compounds have a significantly higher market value compared with that for crude glycerol (88 USD kg⁻¹ or 111 USD L⁻¹). For example, the commercial prices of technical grade acetol (90% purity), natural grade glycidol (96% purity) and reagent grade 2-methyl-2-pentanol (99% purity) are greater than 556, 611 and 7923 USD kg⁻¹, respectively. The commercial prices of 1,2-PD (98% purity) and 1,3-PD (98% purity), produced by electrochemical conversion of glycerol in an acidic electrolyte are 190 USD L⁻¹ and 481 USD kg⁻¹, respectively. Also, the commercial prices of reagent grade acrolein (97% purity) and glyceraldehyde (90% purity), generated under a neutral condition are greater than 150 and 74,657 USD kg⁻¹, respectively. In addition, they have a high market capacity and application in various industries [1].

Table 1. List of added-value chemicals generated by the steady-state CVs of glycerol solution at different initial pH values and their current price and CAS reference number.

Chemical	Initial solution pH			USD (%purity) [36]	[CAS no.]
	pH 1	pH 7	pH 11		
Acetol/ Hydroxyacetone	✓	✓	✓	556.3 kg ⁻¹ (90%) ^a	[116-09-6]
Glycidol	✓	✓	✓	611.3 kg ⁻¹ (96%) ^b	[556-52-5]
2-Methyl-2-pentanol	✓	✓	✓	7923 kg ⁻¹ (99%) ^c	[590-36-3]
3-Methyl-2-pentanone	✓	-	✓	1,527 kg ⁻¹ (99%)	[565-61-7]
2,3-Hexanediol	✓	-	✓	80,960 L ⁻¹ (99%) ^c	[617-30-1]
1,2-Propanediol	✓	-	-	190 L ⁻¹ (>99.5%) ^c	[57-55-6]
1,2-Butanediol	✓	-	-	174.9 L ⁻¹ (>98.0%) ^d	[584-03-2]
1-Isopropoxy-2-propanol	✓	-	-	213,450 kg ⁻¹ (98%) ^c	[3944-36-3]
1,3-Propanediol	✓	-	-	481.8 kg ⁻¹ (98%) ^c	[504-63-2]
1,3-Dioxolane	✓	-	-	165.5 L ⁻¹ (99%) ^c	[646-06-0]
1,3-Dioxolane-4-methanol,2,2-dimethyl	✓	-	-	492.3 kg ⁻¹ (98%) ^c	[100-79-8]
5-Methyl-1-heptanol	✓	-	-	894,000 L ⁻¹ (96%) ^c	[57803-73-3]
2,4-Dimethyl-1,3-dioxane	-	-	✓	10,504 kg ^{-1c}	[766-20-1]
Ethylene glycol isopropyl ether	-	-	✓	65.0 L ⁻¹ (99%) ^c	[109-59-1]
2-Hexanol	-	-	✓	2,630 kg ⁻¹ (>98%) ^c	[626-93-7]
Tetramethylsilane	-	-	✓	2,320 kg ⁻¹ (>99%) ^c	[75-76-3]
4-Methyl-1-hexanol	-	-	✓	104,000 L ⁻¹ (>98%) ^c	[1767-46-0]
Acrolein/acryraldehyde	-	✓	-	150 kg ⁻¹ (97%) ^c	[107-02-8]
4-Pentene-2-ol	-	✓	-	22,344 kg ⁻¹ (99%) ^c	[625-31-0]
Propanoic acid/ Propionic acid	-	✓	-	673.5 L ⁻¹ (>99.5%) ^c	[79-09-4]
3-Pentene-2-ol	-	✓	-	32,607 kg ⁻¹ (96%) ^c	[3899-34-1]
Glyceraldehyde	-	✓	-	74,644 kg ⁻¹ (>90%) ^c	[56-82-6]

^aTechnical grade, ^bNatural grade, ^cReagent grade, ^dPurum grade

3.2 Effect of the initial electrolyte pH on the electrochemical glycerol conversion level and distribution of the products

The variation in the glycerol concentration and conversion during the long-term electrolysis at different initial electrolyte pH values is given as a function of time in Fig. 2. As expected, the glycerol concentration decreased while the glycerol conversion increased with increasing electrolysis time. The highest glycerol conversion was observed in the pH 1 electrolyte, the lowest at pH 7. The glycerol was completely converted within the first 13 h at an initial electrolyte pH value of 1, while the conversion was around 49.4 and 67.6% at an initial electrolyte pH of 7 and 11, respectively. This might be attributed to the different conversion mechanisms in the presence of different H^+ and OH^- concentrations. As outlined in the introduction, the electrolysis of alcohol is a multi-step reaction [23]. The efficiency of the alcohol conversion and product yield depended on the interaction between both the electrode surface and the alcohol molecules and the resulting adsorbed product fragments, as well as the formation of surface oxides [24]. In the case of glycerol, the electrochemical conversion may occur after the adsorption of glycerol on either the oxide-free Pt (Pt) or oxidized Pt (PtO) electrode surface in an acid electrolyte or on the hydroxide-adsorbed Pt (Pt-OH) surface in a basic electrolyte [25, 35, 37]. Besides, the electrooxidation of glycerol to some intermediate species, such as glyceraldehydes, requires only the abstraction of two protons and no adsorbed OH^- is needed [38]. In a basic electrolyte the available OH^- can act as a catalyst to accelerate the dehydration and retro-aldol reaction of glyceraldehyde [39-42], resulting in the variation of glycerol conversion products formed in the presence of different pH conditions.

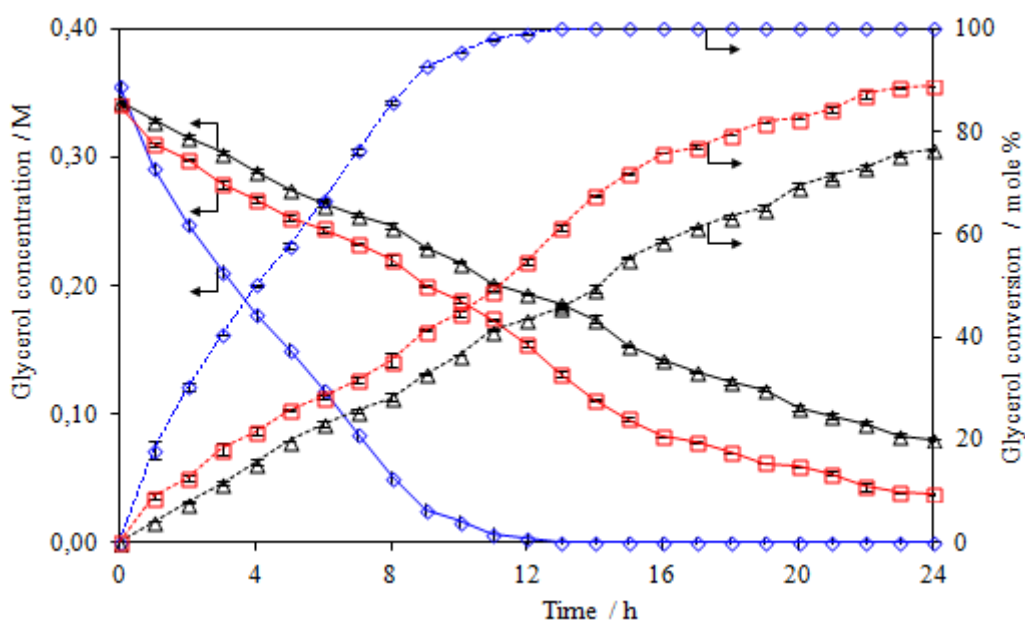


Figure 2. Variation in the (–) glycerol concentration and (···) glycerol conversion by electrochemical conversion at an initial glycerol solution pH of 1 (\diamond), 7 (\triangle), and 11 (\square) at a current intensity of 4.5 A using a Pt electrode.

The initial kinetics of glycerol conversion was calculated using a macro-kinetics model based upon the first-order rate kinetics. The decrease in the glycerol concentration at all three initial pH values was found to fit the model very well over the first 6, 10 and 13 h at pH 1, 11 and 7, respectively, with coefficient of determination (R^2) of greater than 0.987 in all three cases (Fig. 3). The linear plot obtained during the first 6, 13 and 10 h of electrolysis time of the glycerol solution at an initial pH of 1, 7 and 11, respectively, gave a rate constant (k) of 2.95×10^{-3} , 7.95×10^{-4} and $9.20 \times 10^{-4} \text{ min}^{-1}$, respectively.

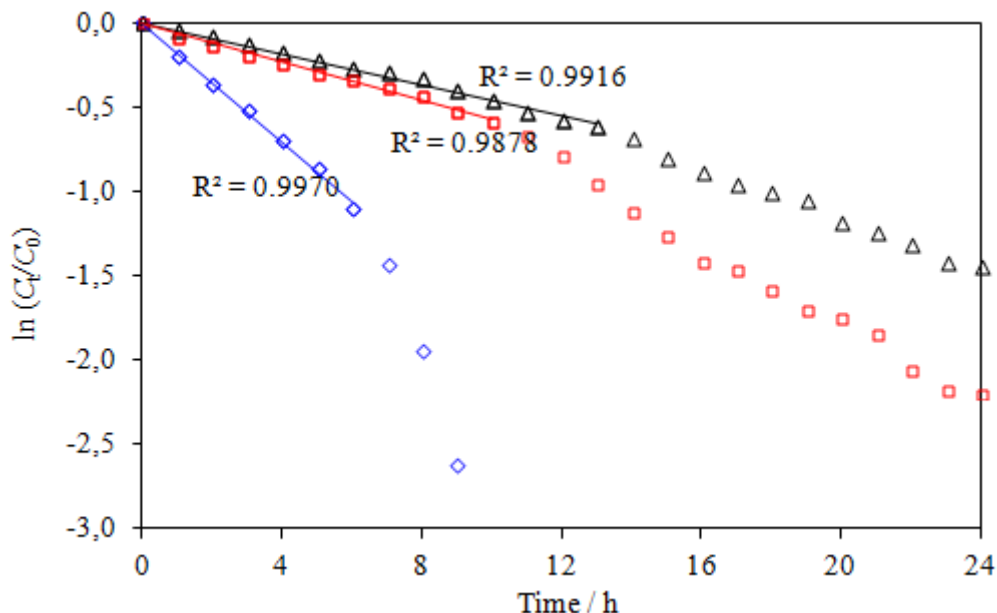


Figure 3. First-order kinetics of the electrochemical conversion of glycerol at an initial glycerol solution pH of 1 (\diamond), 7 (\triangle), and 11 (\square) with a current intensity of 4.5 A using a Pt electrode.

The variation in the yield of the high market value products, as detected by HPLC analysis, during the long-term electrolysis of glycerol in the presence of electrolytes with an initial pH of 1, 7 and 11 is demonstrated in Fig. 4. Glycidol ($\text{C}_3\text{H}_6\text{O}_2$) and acrolein ($\text{C}_3\text{H}_4\text{O}$) were the major reaction products generated at all three initial pH values, although ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and acetol ($\text{C}_3\text{H}_6\text{O}_2$) were produced at both pH 1 and 11. In the strong acidic electrolyte, 1,2-PD and 1,3-PD were also generated at proportionally high levels, but were not found in the neutral and basic electrolytes. The strong acid and basic electrolytes lead to a high level of generated reaction products compared to that obtained with the neutral pH electrolyte. Ethylene glycol was generated after 4 h of electrolysis time in both pH 1 and pH 11 (but not pH 7) electrolytes, implying that the glycerol cannot be directly converted to ethylene glycol. The yield of ethylene glycol then increased, slightly at pH 1 and significantly at pH 11, with further electrolysis time, although in the acidic electrolyte it decreased slightly after 18 h electrolysis and longer, while it continued to increase in the basic electrolyte. The conversion of glycerol to ethylene glycol might involve a two-step reaction; the (i) dehydrogenation of adsorbed glycerol to the intermediate species or glyceraldehyde ($\text{C}_3\text{H}_6\text{O}_3$), and (ii) the cleavage of the

C-C bond of glyceraldehyde to ethylene glycol and methanol (CH₃OH). As previously reported, the production of glyceraldehyde was found to depend greatly on the applied potential and the pH of the electrolyte [25]. The selectivity towards the formation of glyceraldehyde was very high in the acidic electrolyte when the applied potential was chosen before the beginning of the oxidation of the electrode surface. In other words, the dehydration occurred on the oxide-free Pt electrode. In the basic electrolyte, the oxidation of glycerol to glyceraldehyde can occur over the equilibrium oxide-covered Pt (Pt-OH) [25]. The C-C cleavage of the intermediate glyceraldehyde may occur by proton (H⁺) addition in near-critical water without the addition of acid or base [43]. The decrease in ethylene glycerol levels at longer electrolysis times in the acidic electrolyte might be attributed to the electrooxidation of ethylene glycerol to formic acid and glycolic acid [27, 30]. Besides, glyceraldehyde can undergo oxidation or reduction to other products, such as glyceric acid [38].

The yield of acetol was observed after 2 h of electrolysis time in both the acidic and basic electrolytes, but not until after 10–12 h in the neutral electrolyte, and then increased in concentration with increasing electrolysis time (Fig. 4). The generation of acrolein was clearly detected after 7 h and increased with the electrolysis time thereafter in the basic electrolyte. However, in the acidic electrolyte it increased as a function of time and reached its maximum yield (32.2%) within 19 h before decreasing with further electrolysis time (Fig. 4a). The main mechanism can be speculated that, in the presence of electricity, glycerol undergoes adsorption and dehydration on the active site of the Pt electrode [33, 35]. If the 1^o-OH group of glycerol was involved 2,3-dihydroxypropene would be generated and instantaneously transformed to acetol (1-hydroxyl-2-propanone). On the other hand, if the 2^o-OH group of glycerol is involved the enol intermediate species (3-hydroxypropanal) would be formed, which would then rapidly be rearranged to acrolein (acrylaldehyde) [28]. In the acidic electrolyte, these two species are themselves reactive and readily reduced to 1,2-PD and 1,3-PD, respectively. However, their yields were very low during the early period of acrolein and acetol formation, because the rapid C-C bond dissociation can occur at the utilized operating condition [33]. In terms of the yield of acrolein and 1,3-PD (in the acidic electrolyte), a higher yield of 1,3-PD than acrolein was observed during 10–14 h electrolysis. Acrolein was observed from 7 to 8 h and increased up to 19 h before declining with longer times. 1,3-PD appeared from 9 to 10 h and increased in accumulation quickly up to after 19 h electrolysis but then increased only slowly thereafter. Thus, a slower increase in the rate of 1,3-PD accumulation relative to acrolein was observed during 15–18 h of electrolysis time (Fig. 4a). The reduction in acrolein without significant accumulation of 1,3-PD might be due to the reduction of acrolein into 1,2-PD in the heterogeneous system [44]. With respect to the yield of glycidol, it increased instantaneously when the electricity was applied. It is believed that glycidol was obtained from the rearrangement of the glycerol carbonium ion, derived from the protonation of the 2^o-OH group of glycerol [28]. A simplified diagram showing the possible major reaction pathways of glycerol conversion by this electrochemical conversion over a Pt electrode is shown in Scheme 1. These compounds have a potentially important role in the petrochemical industries for fuel and chemical production. However, this technique still needs additional research and development to reliably provide a higher selectivity of any given specific product in order to obtain high quality products that are both economically and operationally feasible.

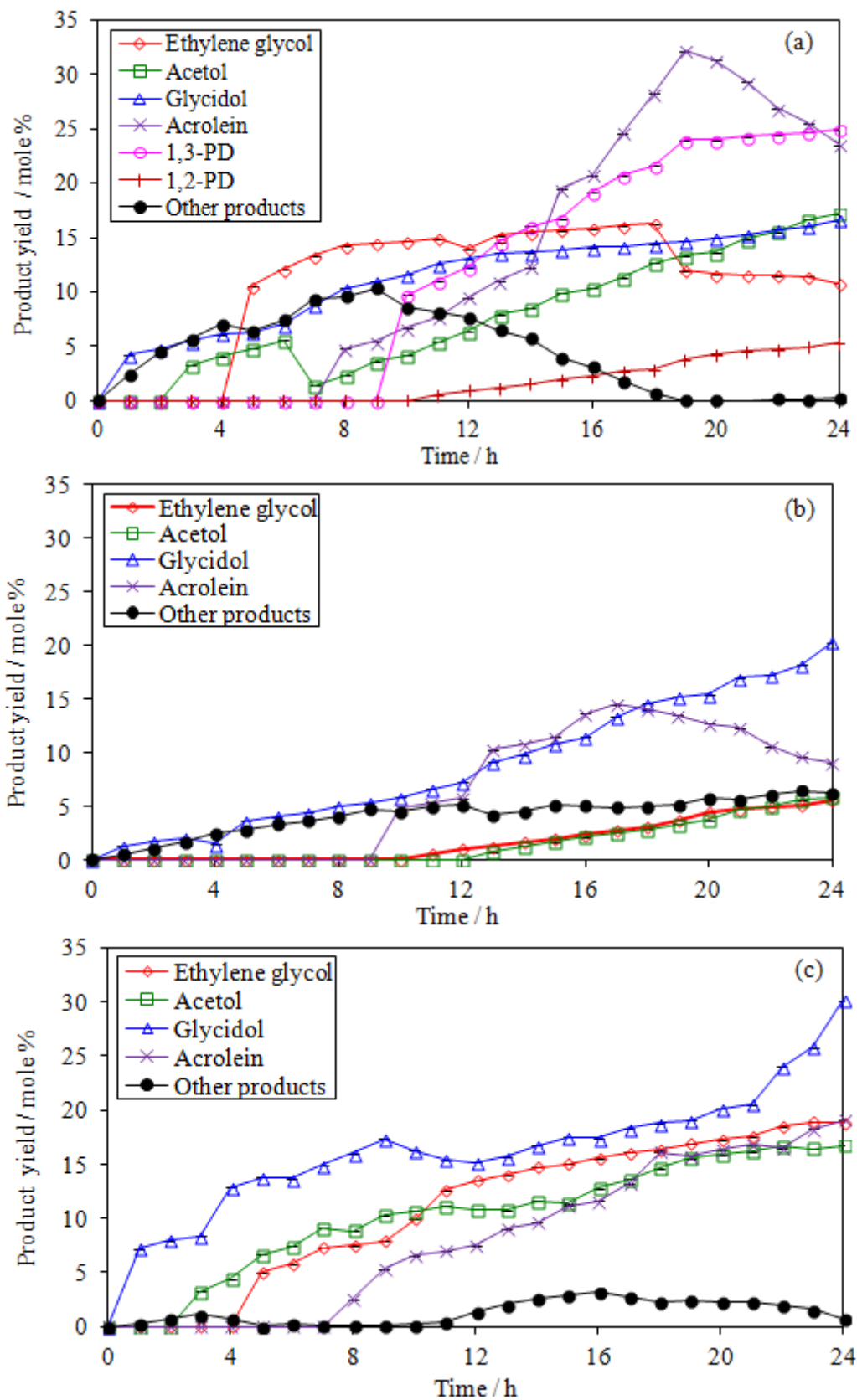
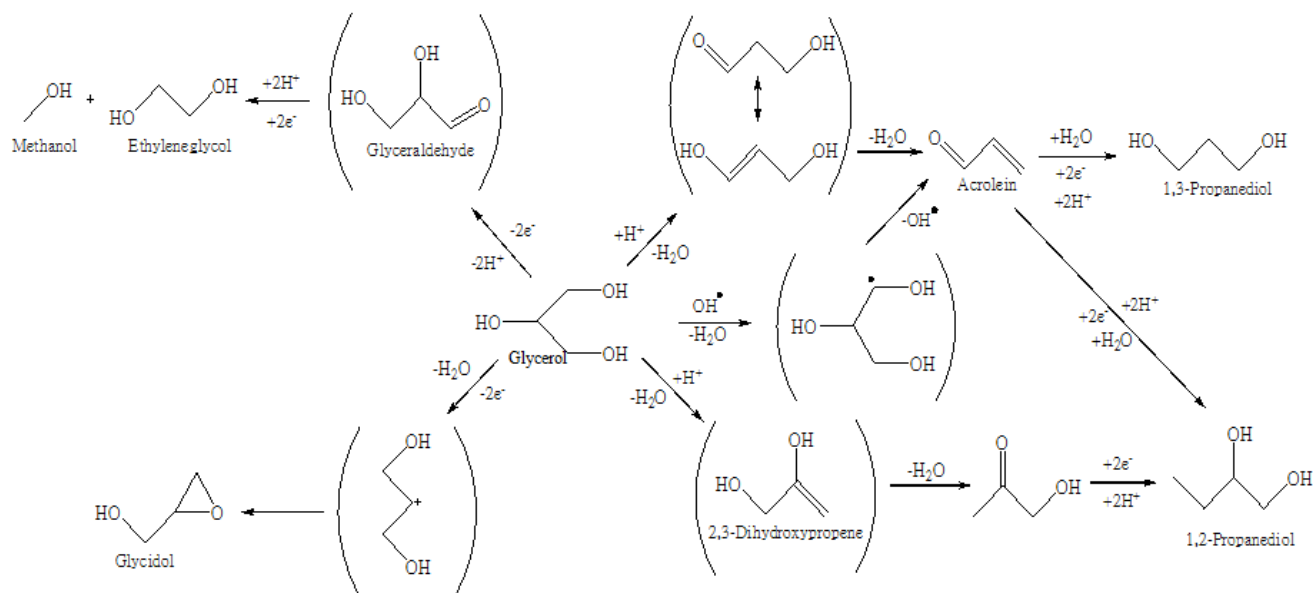


Figure 4. Product distribution following the electrochemical conversion of glycerol at an initial glycerol pH of (a) pH 1, (b) pH 7, and (c) pH 11 with a current intensity of 4.5 A using a Pt electrode.



Scheme 1. Proposed reaction pathways for the electrochemical conversion of glycerol over a Pt electrode

4. CONCLUSIONS

The electrochemical conversion of glycerol to higher value and in-demand chemicals, such as acrolein, 1,2-PD, 1,3-PD and glycidol, was successfully developed in a simple electrochemical system with a Pt electrode. The initial pH of the glycerol electrolyte significantly affected the glycerol conversion and product distribution and yields. Quantitatively, the electrochemical conversion of glycerol was in the order of pH 1 \gg pH 11 > pH 7 with a rate constant of 2.95×10^{-3} , 7.95×10^{-4} and $9.20 \times 10^{-4} \text{ min}^{-1}$, respectively. In a strong acid electrolyte (pH 1), complete glycerol conversion was obtained within 13 h with a product yield of greater than 63.6% and a maximum product yield of 99.99 mol% being obtained after 19 h electrolysis time. This provided a yield of acrolein, 1,2-PD, 1,3-PD, glycidol, ethylene glycol and acetol of 32.2, 3.77, 24.0, 14.7, 12.0 and 13.4 mole %, respectively.

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