This is an aurhor's version published in: http://oatao.univ-toulouse.fr/25851

Official URL:

https://doi.org/10.1016/j.scitotenv.2019.135137

To cite this version:

Rahim, Siti Aqilah Nadhirah Md. and Lee, Ching Shya and Abnisa, Faisal and Aroua, Mohamed Kheireddine and Daud, Wan Ashri Wan and Cognet, Patrick and Peres-Lucchese, Yolande *A review of recent developments on kinetics parameters for glycerol electrochemical conversion – A by-product of biodiesel.* (2020) Science of the Total Environment, 705. 135137. ISSN 0048-9697.

A review of recent developments on kinetics parameters for glycerol electrochemical conversion – A by-product of biodiesel

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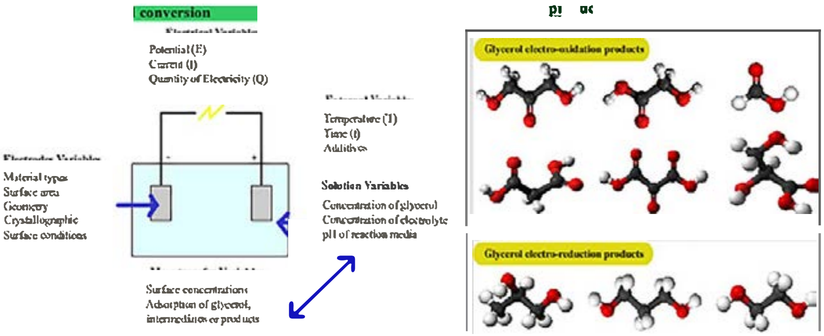
GRAPHICAL ABSTRACT



ABSTRACT

Keywords:
Electrodes materials
pH of electrolyte
Applied potential
Current density
Additives
Temperature

Glycerol is a by product produced from biodiesel, fatty acid, soap and bioethanol industries. Today, the value of glycerol is decreasing in the global market due to glycerol surplus, which primarily resulted from the speedy expansion of biodiesel producers around the world. Numerous studies have proposed ways of managing and treating glycerol, as well as converting it into value added compounds. The electrochemical conversion method is preferred for this transformation due to its simplicity and hence, it is discussed in detail. Additionally, the factors that could affect the process mechanisms and products distribution in the electrochemical process, including electrodes materials, pH of electrolyte, applied potential, current density, temperature and additives are also thoroughly explained. Value added compounds that can be produced from the electrochemical conversion of glycerol include glyceraldehyde, dihydroxyacetone, glycolic acid, glyceric acid, lactic acid, 1,2 propanediol, 1,3 propanediol, tartronic acid and mesoxalic acid. These compounds are found to have broad applications in cosmetics, pharmaceutical, food and polymer industries are also described. This review will be devoted to a comprehensive overview of the current scenario in the glycerol electrochemical conversion, the factors affecting the mechanism pathways, reaction rates, product selectivity and yield. Possible outcomes obtained from the process and their benefits to the industries are discussed. The utilization of solid acid catalysts as additives for future studies is also suggested.

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Contents

1. Introduction

Fossil fuel is essentially the primary source of energy and a key driver of societal progress over the past two centuries. The Energy Information Administration (EIA) has projected the global energy demand increases by 48% from 2012 to 2040. But, fossil fuel resources have depleted and renewable energy appears as the world's fastest growing energy source that increases by 2.6% per year over that period (EIA, 2016). This paradigm happens due to the energy shortage and increase of the environmental concerns such as acid rain, ozone layer depletion and global climate change caused by the exploitation of fossil fuel in the industrialization. In this regard, biogas, bioethanol and biodiesel from renewable fuel have gained spectacular interest in niche markets to replace the fossil fuel (Leung et al., 2010; Simões et al., 2012). Biogas, bioethanol and biodiesel are used to substitute natural gas, petrol and diesel, respectively (Katryniok et al., 2011; Aditiya et al., 2016). During the biodiesel and bioethanol manufactures, crude glycerol is the main by product, which accounts approximately 10% (wt/wt) of total biodiesel and 7 8% (wt/wt) of bioethanol generation (Amorim et al., 2011; Luo et al., 2016). With the rapid production and consumption of these green energy sources, glycerol production has inevitably increased year by year and appeared as an oversupplied waste. Between 2008 and 2012, glycerol generation was increased by 9.3% yearly which was driven mainly from the biodiesel manufacture (Monteiro et al., 2018). Also, it was reported in the OECD report that 42 billion litres of biodiesel are expected produce in 2020 which explains to 4.2 billion litres of glycerol will be generated (OECD, 2011).

The surplus of glycerol waste has been recognized as a serious threat to the biofuel industry associated to the disposal cost, and purification cost. The presence of contaminants may reduce its overall market price (Quispe et al., 2013; Coronado et al., 2014; Luo et al., 2016). Though glycerol is exploited as a raw material in the food, cosmetics and pharmaceutical industries, its production is much higher than the global demand (Ciriminna et al., 2014). In 2007, the commercial value of crude glycerol and purified glycerol in the United States was reduced from $0.25 per pound to $0.05 per pound and $0.70 per pound to $0.30 per pound, respectively (Yang et al., 2012) Glycerol market price was further slumped to approximately zero and even into negative value as manufacturers are forced to pay for the glycerol to be removed for incineration (Gholami et al., 2014). Apart from that, landfilling and burning are the conventional processes that have been used to manage glycerol waste. These techniques are not environmentally friendly due to the uncontrolled release of methane to the atmosphere. Moreover, the leachate formed contaminates the soil and the groundwater, leading to the emission of unpleasant odors, which facilitates the spread of pathogenic microorganisms (Taylor and Allen, 2006; Kong et al., 2016). The poor management of this waste is not only affecting the biofuel market. It also constitutes a high risk to human life and the environment. These issues have prompted the researchers to find a recycling solution for this waste to uphold sustainability which alleviates environmental impact and boosts the biofuel market, simultaneously.

The growth of high value added chemicals from low grade crude glycerol is the only way to improve the glycerol value and replace the disposal and purification costs with a wiser application. Techniques like hydrogenolysis (Dieuzeide et al., 2017; Cai et al., 2019; Xu et al., 2019; Chimentão et al., 2020), dehydration (dos Santos et al., 2019; Jia et al., 2019; Zhang et al., 2019), photocatalysis (Minero et al., 2012; Dodekatos et al., 2018; Mendoza et al., 2019), etherification (D.Bozkurt et al., 2015; Lemos et al., 2018; Liu et al., 2019), selective oxidation (Han et al., 2019; Yan et al., 2019; Zhao et al., 2019), oligomerization (Karam et al., 2016; Galy et al., 2017), carboxylation (Aresta et al., 2006; Narkhede and Patel, 2016; Okoye and Hameed, 2016) and fermentation (Rukowicz and Alejski, 2018; Haosagul et al., 2019; Zhu et al., 2019) have been investigated for glycerol transformation. Yet, recently, the electrochemical conversion technique has shown higher economic interest. This method is highly recommended compared to the methods previously mentioned because of its green process, robustness and simplicity. It is regularly viewed as an eco friendly process since it uses electron as a redox reagent rather than relying on potentially hazardous chemical oxidants and reductants. Despite that, to make the electrochemical technology to be completely green, the electricity employed in it should be from sustainable sources. The electrical power that is presently utilized worldwide is obtained from the combustion of carbon based compounds (i.e.; natural gas and coal). These sources are nonrenewable and hence, promising modern technologies such as wind and solar energies are currently underway to produce the electrical power (EIA, 2016). This development has created an additional benefit for the electrochemical conversion of glycerol as an efficient interconversion of electrical and chemical energy that supports the decarbonisation of the electric grid and offers new opportunities for chemical manufacturing (Orella et al., 2018). Plus, renewable energy sources are now cost competitive with fossil fuel based electricity (0.055$ kWh^{-1}) as the cost generated from wind and solar energies has reduced 67% (to 0.045$ kWh^{-1}) and 86% (to 0.050$ kWh^{-1}), correspondingly, after eight years (Lazard, 2017).

The innovations are not only facilitating low carbon power sources, but they also enhance safety and reduce reactor costs through mild reactions conditions and increase the flexibility of the process through controllable products formation. It has high energy efficiency, and it can be conducted under mild temperature and ambient pressure, without external power supply for the heater and temperature control system (Dai et al., 2017; Orella et al., 2018). This mild operating condition makes electrochemical conversion differs from the thermochemical process. For instance, about 220 °C is required to achieve 85% selectivity of 1,2 propanediol for hydrodeoxygenation reaction while ~86% selectivity of 1,2 propanediol is achievable at 80 °C using the electrochemical technique (Ardila et al., 2017; Lee et al., 2018). The electrochemical process involves two half reactions (reduction and oxidation), which enables the independent optimization of each reaction (Orella et al., 2018). Parameters like electrodes materials, pH of electrolyte, applied potential, current density, temperature and additives have a significant influence on the electrochemical process (Benipal et al., 2017; Da Silva et al., 2017; Han et al., 2018). Several excellent reviews have been carried out on glycerol electrochemical conversion. Simões et al. (2012) provided an overview of glycerol electrochemical conversion principle and highlighted the relevant researches on developed electrocatalysts towards an efficient practice. More recently, Talebian Kiakalaieh et al. (2018) and Houache et al. (2019) emphasized on the latest studies concerning electrocatalysts' nature, structure and composition as factors affecting electro oxidation of glycerol. The recently developed noble metals based and non platinum metals based electrocatalysts were reviewed in their literature. These reviews reveal the state of the art approach in enhancing the products selectivity with one or more metallic catalysts with different geometry, morphology, surface composition and catalyst supports (Talebian Kiakalaieh et al., 2018; Houache et al., 2019). However, their review papers do not provide information on how other parameters affect the mechanism pathway, especially in the formation of the intermediates.

This paper aims to provide a comprehensive review of mechanistic and kinetics perspectives. The kinetics and thermodynamic parameters are not only influenced by the electrodes or electrocatalysts materials. They are also affected by the pH of reaction media, current density, voltage, temperature and additives, which they are thoroughly discussed. An emphasis is placed on both electro oxidation and electro reduction reactions to offer insight towards obtaining high catalytic performance as well as products selectivity and yield at a mechanism pathway. The potential applications of the value added products are also highlighted in this manuscript as they are vital in our global market.

2. Glycerol and value-added chemicals in the market prospects

In 1999, the primary sources of glycerol were from fatty acids (47%), soaps (24%), fatty alcohol (12%) and biodiesel production (9%). Conversely, the percentage of glycerol sources has shifted, and biodiesel industry (64%) has appeared the primary glycerol producer since 2009 (Gholami et al., 2014). Glycerol that obtained through these processes contains high impurities and is known as the crude glycerol. The composition of crude glycerol depends on the reaction conditions during the production processes and the extent of the purification of the crude glycerol. The percentage of glycerol in the crude glycerol ranges from 45% to 80%. Since the variation of crude glycerol composition is huge, it is difficult to generalize its properties. The properties of glycerol have been discussed in detail in the literature (Coronado et al., 2014).

Glycerol is a multi functional compound that could be transformed to >2000 fine chemicals from its crude form (Tan et al., 2013; Okoye et al., 2017). The primary and secondary hydroxyl groups in glycerol structure facilitate its conversion into carboxylic acids, phenolic, aldehydes and ketones compounds. These compounds are commonly used in cosmetics, medicine, polymer, and food industries. The most common oxidation products are glyceraldehyde, dihydroxyacetone, glyceric acid, hydroxypyruvic acid, tartronic acid, mesoxalic acid, glycolic acid, lactic acid and glyoxylic acid. Although some of these products are vastly valuable compounds (like glycolic acid, glyceric acid and lactic acid), others like dihydroxyacetone have a lower price in the market. The valuable compounds like 1,2 propanediol and 1,3 propanediol are the new potential products that have been achieved recently via glycerol electro reduction reaction, where 1,3 propanediol has higher market price than 1,2 propanediol (James et al., 2018; Lee et al., 2018). Some products available from both glycerol electro oxidation and electro reduction reactions with their applications are listed in Table 1.

3. Fundamental reactions

An understanding of the basic chemistry in the electrochemical reaction and its engineering aspect is essential since most of these compounds serve great opportunities in many industries. Fuel cells and electrolysis cells are recently employed for glycerol conversion. Fuel cell technology generates both valuable compounds and electrical energy by glycerol oxidation at anode and oxygen reduction at the cathode (Fig. 1**a**). Whereas, electrolysis lead to the co generation of valuable compounds and hydrogen through glycerol oxidation at anode and water reduction at cathode (Fig. 1**b**) (Simões et al., 2012; Talebian Kiakalaieh et al., 2018). Both reactors can be upgraded to bring higher economic interest to the process. As such, microbial electrochemical cells or bioelectrochemical systems (BES) have penetrated the research area by producing 1,3 propanediol from crude glycerol (Roume et al., 2016). The highest yield of 1,3 propanediol (72%) was achieved from the electro fermentation in the BES which is very close to the 1,3 propanediol yield reported in a mixed microbial culture based glycerol fermentation process. When compared with other conventional heterogeneous catalytic reactors, the operating cost of glycerol electrochemical conversion is cheaper due to the simplicity of the reaction process and the reactor design (Kim et al., 2017a). Glycerol electrochemical reforming also saved approximately 2.1 kWh m ^{3} H_2 of electrical energy and the energy efficiency of glycerol conversion to hydrogen was around 44%. Although 82% of the electricity generated from hydrogen is supplied by glycerol and 18% of the energy came from the electrical energy, the electricity consumption was reduced to 66% from 82% (Marshall and Haverkamp, 2008). Therefore, in terms of economic feasibility, this process has achieved this benchmark and could be brought for upscale study in the future.

Other than a single cell, a two compartment cell is frequently performed through an anion exchange membrane (AEM) that is known as a reversed ionic diffusion migration process or a proton exchange membrane (PEM) which is a direct proton diffusion migration process. Ideally, these membranes must easily transport ions to maintain a high conductivity and a low applied potential between the electrodes when using high currents. They should be low permeability which means with a minimal exchange of solvent and neutral molecules (Frontana Uribe et al., 2010). The difference between these membranes is the charge carrier where hydroxide ions (OH) will migrate through AEM from the cathode to anode whilst the hydrogen ions (H^+) travel through PEM from the anode to cathode to allow the completion of redox catalysis (Fig. 1). The electrons released from the electro oxidation reactions will migrate through the external circuit to complete the loop (Pan

Table 1

. Products available from glycerol electro-oxidation and electro-reduction reactions with their applications.

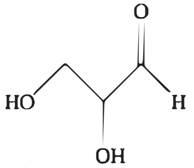
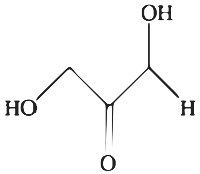
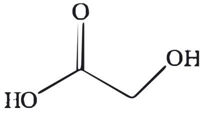
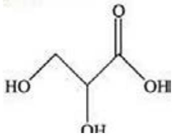
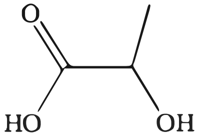
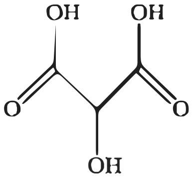
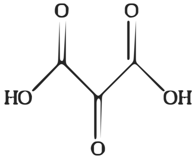
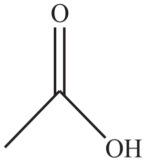
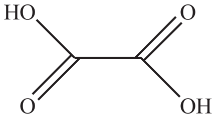
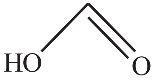
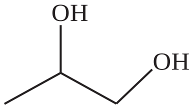
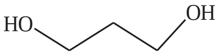
Products	Description	Application	Selling price in USD (% Purity)	References
Glyceraldehyde 	• It is a triose monosaccharide, which is the simplest of all common aldoses and it is known as glyceral. • It is a colorless and sweet crystalline solid, which could be obtained as an intermediate species during glycerol oxidation.	■ Anti-ageing agent in production of advanced glycation end-products (AGEs). ■ A fundamental metabolite, modification and crosslinking of proteins.	170/g (98%)[a]	(Bijvoet et al., 1951; Pinter et al., 1967; Clough, 2014)
Dihydroxyacetone 	• Dihydroxyacetone, also called glycerone, is a simple saccharide (a triose). • It is a ketotriose comprising acetone with hydroxyl substituents at 1 and 3 positions. • It is the parent of the class of glycerones and the simplest member of the class of ketoses.	■ A versatile intermediate to produce other organic compounds and as tanning agent in cosmetics. ■ Antifungal agent and raw material for D, L-serin production, monomer for polymeric biomaterials. ■ As a metabolite for human, Escherichia coli and Saccharomyces cerevisiae metabolite	69/g (97%)[a]	(Petersen et al., 2003; Pagliaro et al., 2007; Bagheri et al., 2015)
Glycolic acid 	• It is a conjugate acid of glycolate and the smallest α-hydroxy acid (AHA) that is known as hydroxyacetic acid or hydroacetic acid. • It is an odorless, hygroscopic, and colorless crystalline solid, which is extremely water-soluble.	■ As an anti-oxidizing agent or chemical peeling product in the cosmetic industries. ■ A precursor for drug synthesis material and biopolymer material production. ■ It is used broadly in the production of biodegradable poly(glycolic acid) (PGA) for ideal packaging material and poly(lactic-co-glycolic acid) (PLGA) for medical applications.	3295/kg (99%)[b]	(Hua et al., 2018)
Glyceric acid 	• It is a conjugate acid of glycerate, and a natural three-carbon sugar acid. • It is a trionic acid, comprising propionic acid substituted at the second and third positions by hydroxy groups.	■ As an intermediate for further oxidation to tartronic acid or mesoxalic acid. ■ It possesses anticholesterol activity and esters of glyceric acid that have antitrypsin activity.	1805/g (99%)[c]	(Katryniok et al., 2011; Hirasawa et al., 2013; Coelho et al., 2018)
Lactic acid 	• It is the conjugate acid of lactate, and an alphahydroxy acid (AHA) because of the existence of carboxyl group, which is adjacent to the OH group. • Lactic acid is synthesized conventionally by chemical synthesis or by fermentation of carbohydrates like glucose, lactose, or sucrose.	■ As the main ingredient in the food industry as a preservative, ascidulant and inhibitor of bacterial spoilage. ■ A raw material in cosmetics, pharmaceuticals, textiles and leather and bio-plastic (PLA) manufactures ■ As an intermediate compound to generate acrylic acid, 1,2-propanediol, pyruvic acid, acetaldehyde and 2,3-pentanedione	402.50/kg (85%)[d]	(Zhang et al., 2016a; Arcanjo et al., 2017; Oberhauser et al., 2018)
Tartronic acid 	• It is a conjugate acid of tartronate and a dicarboxylic acid that is known as 2-hydroxymalonic acid. • It is a malonic acid substituted by a hydroxy group at the second position and its derivative, 2-methyltartronic acid is an isomalic acid. • Tartronic acid is a conjugate acid of ahydroxymalonate and a hydroxymalonate (1-).	■ As a drug-delivery agent in the treatment of diabetes and osteoporosis diseases. ■ As an anti-corrosive and protective agent which its role as an oxygen scavenger helps to prevent the oxidative decomposition in the food industry and corrosion in boilers or other high temperature applications. ■ As an intermediate compound to generate mesoxalic acid via catalytic oxidation technique.	1564/g (97%)[c]	(Caselli et al., 1997; Tian et al., 2016; Coelho et al., 2018)
Mesoxalic acid 	• It is a conjugate acid of mesoxalate that is known as ketomalonic acid or oxomalonic acid. • Mesoxalic acid is both a ketonic acid and a dicarboxylic acid, which voluntarily loses two protons to produce mesoxalate, a divalent anion $C_3O_5^{2}$	■ As a precursor in the synthesis of 4-chlorophenylhydrazone mesoxalic acid which is known to be an anti-HIV agent.	140/g (98%)[c]	(Davis et al., 2000; Ciriminna and Pagliaro, 2004)

Table 1 (*continued*)

Products	Description	Application	Selling price in USD (% Purity)	References
Acetic acid 	• It is a conjugate acid if acetate that is known as ethanoic and methane carboxylic acid. • It is a weak acid and the most vital synthetic carboxylic acid. • In its pure/undiluted form, it is called glacial acetic acid, a colorless liquid with a pungent and strong smell, which characterizes the odor of vinegar.	■ Production of vinegar, antifungal, antibacterial, inhibition of carbohydrate, metabolism, synthesis of chemical compounds like vinyl acetate monomer, ester and acetic anhydride. ■ Involve in manufacturing of perfume, dyes and inks, organic compounds purification, antiseptic against staphylococci, pseudomonas, streptococci, enterococci and others. ■ Involve in screening of cervical cancer, outer ear infections treatment.	62.60/L (99%)[b]	(Staudt et al., 2000; Dibb and Arsenault, 2002; Fornaro and Gutz, 2003)
Oxalic acid 	• It is a conjugate of oxalate and the simplest dicarboxylic acid. • It is a colorless crystalline that forms a colorless solution in water.	■ Cleaning agent including sterilizing of household articles, rest removal, cleaning of kitchen skins, bathtubs and counters. ■ Detergents and bleaches additive, mineral processing mechanisms, bleaching agent in textile industry, purification and dilution of certain chemicals.	93.70/kg (98%)	(Simoneit, 2004; Önal, 2011)
Formic acid 	• It is a conjugate of formate ion that is called methanoic acid. • It is a strong electrolyte, a liquid fuel at room temperature and the simplest form of carboxylic acid. • It is an important intermediate in chemical synthesis and could occur naturally, particularly in some ants.	■ Fuel in fuel cells, reducing agent and environmental benign runway anti-icing (formic acid salts). ■ It is an intermediate in synthesis of some of organic compounds, finishing, and grass silage in Europe. ■ Used in food additives and leather tanning in Asia.	146/L (98)[e]	(Behr et al., 2008; Aslam et al., 2012)
1,2-Propanediol 	• It is known as propylene glycol, is a colorless, odorless, clear, and viscous liquid with slightly sweet taste.	■ Used in unsaturated polyester resins, pharmaceutical products, food, cosmetics, liquid detergents, tobacco, flavourings and scents, personal hygienic products and paints preparation. ■ As anti-freezing and de-icing agents.	298/kg (99%)[b]	(Ardila et al., 2017; Dieuzeide et al., 2017)
1,3-Propanediol 	• It is a diol compound that similar with 1,2-propanediol properties. • It is also a colorless and viscous liquid miscible with water.	■ Used in cosmetics, lubricants and medicines. ■ As intermediate compound in the polymers production (polyesters, polyethers, polyurethanes and polytrimethylene terephthalate (PTT)).	1115/kg (98%)[c]	(Waszak et al., 2016; Rukowicz and Alejski, 2018; Vivek et al., 2018)

[a] HPLC.

[b] ReagentPlus®.

[c] Aldrich.

[d] Natural grade.

[e] ACS reagent adopted from SigmaAldrich.

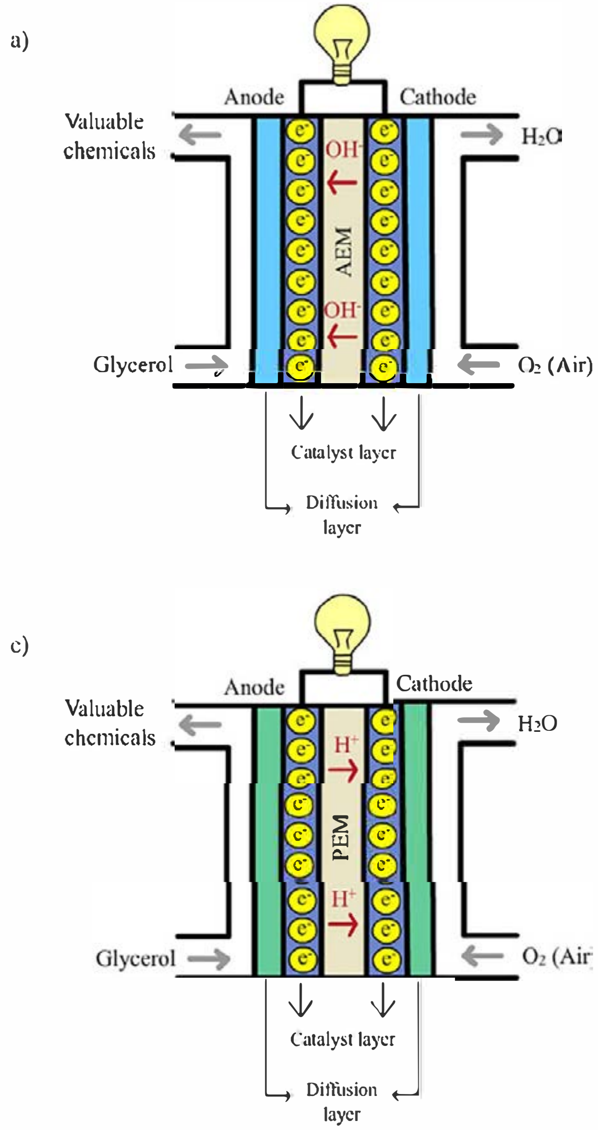


Fig. 1. Working principles of a) AEM-fuel cell, b) AEM-electrolysis, c) PEM-fuel cell and d) PEM-electrolysis (Marshall and Haverkamp, 2008; Simões, 2012; Pan et al., 2018).

et al., 2017). These electrons have been successfully used to convert glycerol into oxidized (like glyceraldehyde and glyceric acid) and reduced (like 1,2 propanediol and 1,3 propanediol) compounds without using any stoichiometric chemical oxidant (like H_2O_2 and O_2) or reductant (like H_2) (Kim et al., 2014; Nakagawa et al., 2018). The basic products formation through this redox catalysis with both reactors have been discussed in the literature (Simões et al., 2012).

However, the mechanistic studies of glycerol remained difficult because of the complexity arising from hydroxyl groups and the presence of different electrocatalysts (Nimlos et al., 2006). The limited knowledge of how the addition and removal of hydroxyl groups or oxygen species in the electrochemical conversion provoke the need for mechanistic and kinetics studies of glycerol reactions. By understanding the precise mechanism and reaction kinetics, process optimization and design becomes easier. This understanding has propelled the search for a more efficient path way for the formation of some specific value added compound during the last few years (Kongjao et al., 2011). In this context, the mechanism and the rate at which glycerol electrochemical conversion proceeds depend on various kinetics and thermodynamic parameters (like electrodes characteristics, pH of the solution, current density, applied potential, additives and temperature). These parameters must be optimized to achieve high selectivity and yield of desired products. The influences of these parameters are studied, and their limits for specific reactions are determined.

4. Effect of parameters on mechanism pathways and reaction performances

The mechanism pathways and reaction kinetics can be influenced by overpotential, glycerol conversion, selectivity and yield of desired products, which could alter reaction parameters like activation energy barrier to stimulate fast molecular collision and surmount the binding energies of the reactants. For instance, an increase in temperature from 27 °C to 80 °C could accelerate the C C bond breakage, hence, converting glycerol into glycolic acid (Lee et al., 2019a). Lee et al. (2019a) reported high glycolic acid yield (66.1%) with a selectivity of 72% after 6 h of reaction at 80 °C. Besides, the glycerol/catalyst molar ratio is a crucial parameter to attain high glycerol conversion and products selectivity (Kim et al., 2017a). Glycerol conversion, yield and selectivity of desired products can be calculated using Eqs. (1), (2) and (3), respectively.

Table 2
Electrodes used in glycerol electro-oxidation and electro-reduction, reaction conditions, glycerol conversion, products selectivity and yield.

Electrode		Reaction parameters							Results			References
WE (A)	CE (C)	Electrolyte	Additives	Current onset (A)	Voltage onset (V)	Temperature (°C)	Stirring speed (rpm)	Reaction time (h)	Selectivity (%)	Yield (%)	Glycerol conversion (%)	
Major product: Glyceraldehyde												
Pt/C	Pt wire	0.1 M glycerol + 0.5 M H_2SO_4	–	–	0.697 vs. SHE	60	–	70	48.8	–	34.2[a]	(Kim et al., 2014)
Pt	Pt	0.1 M glycerol + 0.1 M NaOH	–	–	0.4 vs. RHE	–	–	–	100	–	–	(Kwon et al., 2011b)
Pt	Pt	0.1 M glycerol + 0.5 H_2SO_4	–	–	0.4 vs. RHE	–	–	–	100	–	–	(Kwon et al., 2011b)
Pt	Pt	0.1 M glycerol + 0.1 M NaOH	–	–	0.79 vs. RHE	25	–	28	88	–	49	(Roquet et al., 1994)
Pt	Pt	0.1 M glycerol + 0.1 M $HClO_4$	–	–	0.75 vs. RHE	25	–	28	97	–	49	(Roquet et al., 1994)
Pt	Pt	0.1 M glycerol + 0.1 M $HClO_4$	–	–	1.30 vs. RHE	25	–	28	56	–	49	(Roquet et al., 1994)
Pd NCs	Pt	0.5 M glycerol + 0.5 M KOH	–	–	−0.4 vs. SCE	–	–	–	61.2	–	–	(Zhou and Shen, 2018)
Ti-RuO_2	Pt	0.25 M glycerol + 0.5 M NaCl	–	–	2.5 vs AgCl/Cl	25	–	2	85	–	>10	(James et al., 2018)
Ti-RuO_2	Pt	0.25 M glycerol + 0.5 M HCl	–	–	2.5 vs AgCl/Cl	25	–	2	60	–	30	(James et al., 2018)
Pb	Ti-RuO_2	0.25 M glycerol + 0.5 M KCl	–	–	−1.8 vs AgCl/Cl	25	–	4	55	–	>10	(James et al., 2018)
Pb	Ti-RuO_2	0.25 M glycerol + 0.5 M HCl	–	–	−1.8 vs AgCl/Cl	25	–	4	75	–	30	(James et al., 2018)
Zn	Ti-RuO_2	0.25 M glycerol + 0.5 M NaCl	–	–	2.5 vs AgCl/Cl	25	–	2	75	–	>10	(James et al., 2018)
Major product: Dihydroxyacetone												
Pt	Pt	0.3 M glycerol + pH 1.0	1 mM TEMPO	0.14A/cm^2	–	25	–	24	–	57.2	100	(Saila and Hunsom, 2015)
Pt	Pt	0.3 M glycerol + pH 1.0	3 mM TEMPO	0.14A/cm^2	–	25	–	24	–	65.0	100	(Saila and Hunsom, 2015)
Pt	Pt	0.3 M glycerol + pH 1.0	5 mM TEMPO	0.14A/cm^2	–	25	–	24	–	69.2	100	(Saila and Hunsom, 2015)
Pt_4Au_6@Ag	Pt	0.5 M glycerol + 0.5 M KOH	–	–	1.1 vs. Hg/HgO	–	–	–	77.1	–	–	(Zhou et al., 2019a)
3D nanoporos PtAg skeleton	Pt	0.5 M glycerol + 0.5 M KOH	–	–	0.7 vs. RHE	–	–	1	82.6	–	–	(Zhou et al., 2019b)
3D nanoporos PtAg skeleton	Pt	0.5 M glycerol + 0.5 M KOH	–	–	0.9 vs. RHE	–	–	1	61.5	–	–	(Zhou et al., 2019b)
3D nanoporos PtAg skeleton	Pt	0.5 M glycerol + 0.5 M KOH	–	–	1.0 vs. RHE	–	–	1	79.2	–	–	(Zhou et al., 2019b)
3D nanoporos PtAg skeleton	Pt	0.5 M glycerol + 0.5 M KOH	–	–	1.3 vs. RHE	–	–	1	79.8	–	–	(Zhou et al., 2019b)
PtSb/C	Pt wire	0.1 M glycerol + 0.5 M H_2SO_4	–	–	0.797 vs. SHE	60	400	10	68.1	61.4	90.3	(Lee et al., 2016)
PtSb/C	Pt/C	0.1 M glycerol + 0.5 M H_2SO_4	–	–	0.35–0.55 vs. RHE	Room T	–	–	80	–	–	(Kwon et al., 2014a)
PtBi/C	Pt/C	0.1 M glycerol + 0.5 M H_2SO_4	–	–	0.4 vs. RHE	Room T			100	0.2 mM	–	(Kwon et al., 2012)
Glassy carbon	Pt	0.05 M glycerol + 0.2 M bicarbonate (pH 9.1)	15% mol TEMPO (0.0075 M)	–	1.1 vs. Ag/AgCl	25	–	200	35	25	–	(Ciriminna et al., 2006)
Major product: Glycolic acid												
Pt	CBAC	0.3 M glycerol + Acidic medium	9.6% (w/v) Amberlyst-15	2.0	–	80	–	6	70	66.1	90	(Lee et al., 2019b)
Pt/GNS	Pt	0.5 M glycerol + 0.5 M KOH	–	–	0.2 vs. SCE	60	–	2	65.4	–	–	(Zhou et al., 2018)
Au	Pt	0.1 M glycerol + 0.1 M NaOH	–	–	1.6 vs. RHE	–	–	–	50	–	–	(Kwon et al., 2011b)
Au/C	Pt	0.5 M glycerol + 0.5 M NaOH	–	–	0.1 vs. Ag/AgCl	Room T	–	2	43.98	–	–	(Thia et al., 2016)
Au/CNT	Pt	1.0 M glycerol + 4.0 M KOH	–	–	1.6 vs. RHE	Room T	–	3	80	–	43	(Zhang et al., 2012b)
Au/CNT	Pt	1.0 M glycerol + 2.0 M KOH	–	–	1.6 vs. RHE	Room T	–	3	85	–	34	(Zhang et al., 2012b)
Au/CNT	Pt	1.0 M glycerol + 1.0 M KOH	–	–	1.6 vs. RHE	Room T	–	3	81	–	26	(Zhang et al., 2012b)
Au/CNT	Pt	1.0 M glycerol + 0.5 M KOH	–	–	1.6 vs. RHE	Room T	–	3	79	–	16	(Zhang et al., 2012b)
Au/CNT	Pt	2.0 M glycerol + 2.0 M KOH	–	–	1.6 vs. RHE	Room T	–	3	78	–	19	(Zhang et al., 2012b)
Au/CNT	Pt	0.5 M glycerol + 2.0 M KOH	–	–	1.6 vs. RHE	Room T	–	3	87	–	29	(Zhang et al., 2012b)
Pd (Ag/Pd)	Pt	0.1 M glycerol + 1 M KOH	–	–	−0.1 vs. Hg/HgO	Room T	–	6	–	70	–	(Inoue et al., 2018)
Major product: Glyceric acid												
Pt/C	Pt wire	0.1 M glycerol + 0.5 H_2SO_4	–	–	1.097 vs. SHE	60	–	70	79.9	87	91.8[a]	(Kim et al., 2014)
Pt/C	Pt wire	0.1 M glycerol + 0.5 M H_2SO_4	–	–	0.897 vs. SHE	60	–	70	47.4	69	68.6[a]	(Kim et al., 2014)
Pt/C	Pt wire	0.1 M glycerol + 0.5 M H_2SO_4	–	–	1.0 vs. SHE	60	–	70	–	80	10[b]	(Kim et al., 2014)
Pt	Pt	0.1 M glycerol + 0.1 M NaOH	–	–	1.6 vs. RHE	–	–	–	100	–	–	(Kwon et al., 2011b)
PtNi/GNS	Pt	0.5 M glycerol + 1.0 M KOH	–	–	0.1 vs. SCE	60	–	2	47.7	–	–	(Zhou et al., 2018)
PtRhNi/GNS	Pt	0.5 M glycerol + 1.0 M KOH	–	–	−0.4 vs. SCE	60	–	2	55	–	–	(Zhou et al., 2018)

(*continued on next page*)

Table 2 (*continued*)

Electrode		Reaction parameters							Results			References
WE (A)	CE (C)	Electrolyte	Additives	Current onset (A)	Voltage onset (V)	Temperature (°C)	Stirring speed (rpm)	Reaction time (h)	Selectivity (%)	Yield (%)	Glycerol conversion (%)	
Pt_5Ru_5/C		0.1 M glycerol + 0.5 M H_2SO_4	–	–	1.1 vs. SHE	60	–	7	58.7	–	–	(Kim et al., 2017b)
Au	Pt	0.1 M glycerol + 0.1 M NaOH	–	–	0.8 vs. RHE	–	–	–	100	–	–	(Kwon et al., 2011b)
Au-P4P/G	Pt	0. 5 M glycerol + 0.5 M NaOH	–	–	0.2 vs. Hg/HgO	Room T	–	10	68.6	–	52.5	(Wang et al., 2015)
Au-P4P/rGO	Pt	0. 5 M glycerol + 0.5 M NaOH	–	–	0.2 vs. Hg/HgO	Room T	–	10	57.4	–	52.5	(Wang et al., 2015)
Au-PmAP	Pt	0.5 M glycerol + 0.5 M NaOH	–	–	0.2 vs. Hg/HgO	Room T	–	10	42.2	–	52.5	(Wang et al., 2015)
Pd	Pt	0.1 M glycerol + 1.0 M KOH	–	–	−0.1 vs. Hg/HgO	Room T	–	6	–	56	–	(Inoue et al., 2018)
Major product: Lactic acid												
$AuPt_{0.15}$	Graphite	0.5 M glycerol + 1.0 M KOH	–	–	0.45 Vs. Hg/HgO	Room T	–	12	73	–	29.50	(Dai et al., 2017)
$AuPt_{0.29}$	Graphite	0.5 M glycerol + 1.0 M KOH	–	–	0.45 Vs. Hg/HgO	Room T	–	12	61	–	28.80	(Dai et al., 2017)
$AuPt_{0.64}$	Graphite	0.5 M glycerol + 1.0 M KOH	–	–	0.45 Vs. Hg/HgO	Room T	–	12	60	–	27.10	(Dai et al., 2017)
$AuPt_{0.90}$	Graphite	0.5 M glycerol + 1.0 M KOH	–	–	0.45 Vs. Hg/HgO	Room T	–	12	69	–	16.08	(Dai et al., 2017)
Pt	Graphite	0.5 M glycerol + 1.0 M KOH	–	–	0.45 Vs. Hg/HgO	Room T	–	12	50	–	10.70	(Dai et al., 2017)
Co-DPPE	Ni	250 mM glycerol + 1.0 M NaOH	–	1.8 mA/cm^2	–	60	400	48	45	–	85	(Lam et al., 2017)
Diamond coated	Pt	0.3% (w/w) glycerol + 3.6% (w/w) $Al_2(SO_4)_3$	–	60 A/cm^2	–	55	–	18	–	90	5–10	(Lux et al., 2010)

SHE: Standard hydrogen electrode, RHE: Reversible hydrogen electrode and SCE: Saturated calomel electrode.

[a] Batch reactor.

[b] Continuous reactor.

Glycerol conversion (%)

$$\frac{\text{Amount of glycerol converted (in C mole)}}{\text{Total amount of glycerol in reactant (in mole)}} \times 100\% \tag{1}$$

Product yield (%)

$$\frac{\text{Amount of product (in C mole)}}{\text{Total amount of glycerol in reactant (in mole)}} \times 100\% \tag{2}$$

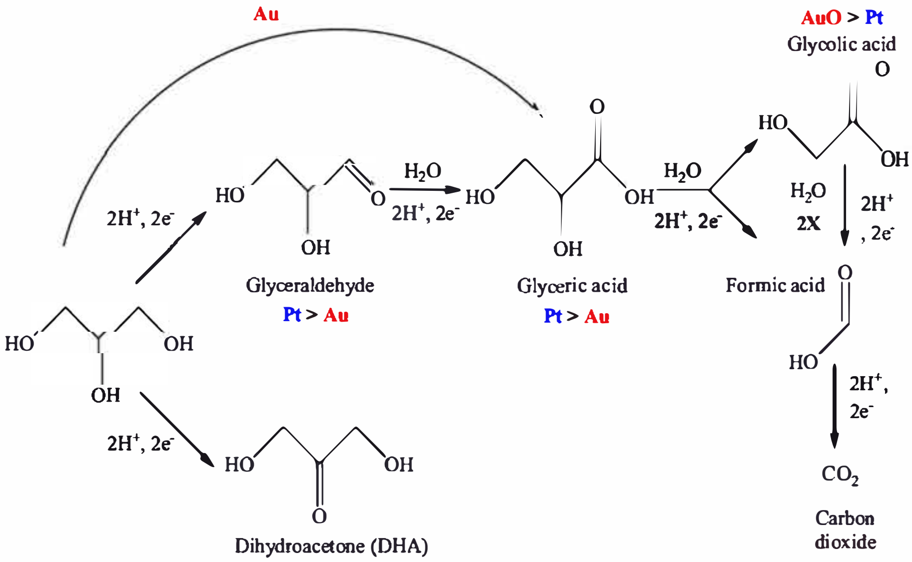
Product selectivity (%)

$$\frac{\text{Amount of product (in C mole)}}{\text{Sum of all the products (in mole) in liquid phase}} \times 100\% \tag{3}$$

Several studies speculated that glycerol electrochemical conversion does not involve external mass transfer limitation. This assumption can be validated using appropriate kinetics and thermodynamic studies of the process. For instance, the kinetics of both electro oxidation and electro reduction reactions must be investigated, and the effect of the process parameters must be explored and optimized. By doing this, the optimum yield and selectivity of desired products could be determined. Table 2 presents various types of electrodes used in their corresponding reaction conditions, glycerol conversion, selectivity and yield of products. Depending on the electrodes and reaction conditions (pH of electrolyte, temperature, applied potential and current density onset), either primary or the secondary hydroxyl group of glycerol can be oxidized to glyceraldehyde and dihydroxyacetone, respectively. A variation of electrode potential in the process can manipulate the size activation energy barrier and subsequently control the products selectivity. This electrode potential adjustment is related to the Gibbs free energy ($\Delta G = nF\Delta E$), where ΔG is the Gibbs free energy of reaction or adsorption, ΔE is the electrode potential, n is the number of electrons, and F is Faraday's constant (96485.34 C/mol). The electrode potential influences the Gibbs chemisorption energy of the products if the electrocatalytic process contains an adsorbed product. Hence, the electrode potential control in the electrocatalytic system may be used to manipulate and tune the relative rates of competing for electrocatalytic processes and the products selectivity. Normally, the effect of each parameter on the reaction is determined when all the parameters are kept constant while varying the parameter under investigation. The results are then validated using kinetic rate laws or other voltammetry, in situ spectroscopy, online chromatography and computational techniques.

4.1. Electrodes materials

Up to now, noble metals such as Pt, Au and Pd monometallic catalysts are the most active in the electro catalytic process. The efficiency of glycerol conversion and product yield is dependent on the interaction between the electrode surface and the glycerol molecule (Gomes and Tremiliosi Filho, 2011). On monometallic catalysts, it is easy to oxidize one of the hydroxyl groups from glycerol and achieve a high yield of desired products (Carrettin et al., 2002). Pt is known to be the only material that is active for the initiation of glycerol oxidation in both acidic and alkaline media. In contrast, Pd and Au are more active for the oxidation of glycerol in alkaline than in acidic media. Kwon et al. (2011b) reported the significant difference in electro oxidation of glycerol on polycrystalline gold (Au) and platinum (Pt) electrodes. Their report shows that only Pt electrode showed remarkable electro catalytic activity in both alkaline and acidic media, while Au electrode became inactive in acidic media for glycerol (Kwon et al., 2011b). The selectivity of glyceric acid was higher in the alkaline medium compared to the neutral and acidic media. As shown in the proposed mecha



Scheme 1. Mechanism of glycerol oxidation on platinum and gold electrodes in alkaline medium (Kwon et al., 2011b).

nism (Scheme 1), on Pt electrode, glycerol was oxidized to glyceraldehyde (approximately to 100% selectivity) at 0.4 V vs. RHE and further oxidized to glyceric acid with 40% selectivity at 0.6 V vs. RHE and 100% selectivity at 1.6 V vs. RHE. Nonetheless, on Au electrode, glycolic acid (45% selectivity) and formic acid (45% selectivity) were formed via C C bond cleavage from glyceric acid after 0.85 V vs. RHE and the selectivity of glycolic acid was 50% at the 1.6 V vs. RHE. The rapid glyceric acid formation was because the increase overpotential on Au electrode has allowed the formation of surface oxide on Au compared Pt electrode which eventually led to the formation of glycolic and formic acids in alkaline medium. Yet, the durability and electrocatalysts cost has been identified as the most important issue in this technology. Durability is one of the major difficulties to have an electrochemical conversion process accepted as a viable commercial product. Electrocatalysts degradation mechanisms may depend on factors like potential, temperature, humidity, contaminants and carbon support stability (Wu et al., 2008).

In this regard, many efforts have been taken to implement the idea of using cost effective non noble metals electrodes or reducing the utilization of expensive electrodes like Pt electrocatalysts. Although Pt and Pt based electrodes have been recognized as the best electrocatalyst in electro oxidation at low temperatures in both fuel and electrolysis cells; however, Pt can be more easily contaminated and more expensive compared to other noble metals (Sankar et al., 2009). The adsorbed species such as carbon monoxide (CO) and aldehydes on Pt catalyst will block the surface and further oxidation is only allowed with the presence of adsorbed OH species (Petukhov et al., 1998). It was reported Pt (1 1 1) facets had better resistance to these poisoning species compared to those of Pt (1 0 0) and Pt (1 1 0) facets owing to the weaker binding strength with the intermediates (Gomes and Tremiliosi Filho, 2011). Therefore, Pt catalyst loading in the electrode needs to be reduced and its durability must be improved. The combination of noble metals with either low cost or earth abundant metals from d group (i.e.; Au, Ag, Ni, Ru) and p group (In, Bi, Sn, Pb, Sb) does not only reduce the onset potential and production cost, it also improve the catalytic activity and alter the mechanism pathways to more selective reactions (Ferreira et al., 2013; Serov et al., 2013; Hasa et al., 2015; González Cobos et al., 2016; Silva et al., 2016; Zhang et al., 2016b; Garcia et al., 2017b; Kim et al., 2017b; Araujo et al., 2019; Zhou et al., 2019a). The electrodes particle size also gives significant impacts on the glycerol electrochemical reactions. As such, the small gold particles of Au/C catalyst exhibited the highest mass activities and at least twice active than the large gold particles in the alkaline medium. It also results in lower glycerol oxidation onset potentials which are at least 100 mV vs. Hg/HgO earlier than the large gold particles of Au/C catalyst. (Padayachee et al., 2014). But, when the gold particles of Au/C catalyst were too small, they became unstable and are estimated to have grown by at least 2 nm with repetitive cycling in alkaline medium.

The catalytic activity of the electrodes also could be enhanced by modifying their surface with different surface composition, shape, catalysts supports, geometry and morphology or application of bi or multi metallic electrocatalysts since they are more active, more selective, and less prone to deactivation than monometallic electrocatalysts (Rousseau et al., 2006; Beltrán Prieto et al., 2013). The electrocatalysts deactivation could be avoided by the bifunctional mechanisms provided by bi or multi metallic catalysts (Iwasita, 2002). When two noble metals electrodes were combined, high selectivity (73%) of lactic acid was obtained on AuPt$_{0.15}$ electrode in 1 M KOH medium instead of glyceric acid and glycolic acid. It was proposed glycerol is oxidized to glyceraldehyde and dihydroxyacetone through deprotonation of glycerol. The deprotonation of glycerol or the abstraction of hydroxide ions can occur with two steps which are (i) base catalyzed oxidation to dihydroxyacetone and (ii) metal catalyzed oxidation (Zope et al., 2010; Kwon et al., 2011a). However, lactic acid was only formed when dihydroxyacetone went through base catalyzed dehydrogenation to 2 hydroxypropenal or pyruvaldehyde and followed by Cannizzaro rearrangement. The enrichment of Au on AuPt$_{0.15}$ electrode has led to the oxidation of secondary alcohol, formed DHA and subsequently produced lactic acid with 73% selectivity (Dai et al., 2017). Formation of this DHA intermediate could be achieved either on bi metallic (AuPt electrode) or tri metallic electrocatalysts (Pt$_4$Au$_6$@Ag electrode) as long as the Au catalyst is slightly higher than Pt catalyst (Zhou et al., 2019a). In Zhou et al. (2019a) work, Pt$_4$Au$_6$@Ag exhibited higher DHA selectivity (77.1%) compared to the Pt$_6$Au$_4$@Ag at 1.1 V vs. Hg/HgO using a similar basic medium (0.5 M KOH). While Zhou and Shen (2018) reported Pd@Pt NCs electrode selectively produced glyceraldehyde in 0.5 M KOH and subsequently electro oxidized into glyceric acid which differs from Dai et al. (2017) and Zhou et al. (2019a) results.

From CV result, Pd@Pt NCs electrode has the highest current density (3.22 mA cm^{-2}) which is 3.5, 4.8 and 1.5 times from the conventional Pd/C, Pt/C and Pd NCs catalysts (Zhou and Shen, 2018).

Gomes et al. (2014) and Inoue et al. (2018) have also replaced Pt with Au catalyst and Pd catalysts, respectively, to encounter the poisoning issue and silver (Ag) was introduced on their catalysts. Ag has no activity toward glycerol reactions but, the introduction of Ag on both Au and Pd catalysts has greatly enhanced the activity and selectivity of desired products at relatively low potentials (Gomes et al., 2014; Inoue et al., 2018). Based on *in situ* infrared reflectance absorption spectra (IRAS) and high performance liquid chromatography (HPLC) results, glycerate and glycolate were obtained as major products on both Pd and Pd (Ag/Pd) electrode at -0.1 V vs. Hg/HgO. On Pd electrode, glycerate (56%) has a higher yield than glycolate (35%) while the formation of glycolate (70%) was favored than glycerate (25%) only on Pd (Ag/Pd) electrode (Inoue et al., 2018). This result revealed the modification of Ag on Pd electrode facilitated the C–C bond cleavage to glycolic acid similar to the presence of Ag on Au electrode which favoring the C–C–C bond breaking, as evidenced by the selective formation of formic acid (Gomes et al., 2014; Inoue et al., 2018). It happened because of the electronic modification that will change the adsorption strength of adsorbates on the Au and Pd surfaces and eventually lead to lower onset potential. However, the excessive addition of Ag content caused the active site of Pd to be more covered by Ag catalyst and reduced the glycerol conversion and power density as investigated by Benipal et al. (2017). They found Pd catalyst favour deprotonation of alcohol in 1.0 M KOH medium while Ag catalyst helps to promote intermediate aldehyde oxidation and the breaking of C–C–C bond to C_2 compounds. As a result, when Ag content increased, the deeper C–C bond cleavage from C_3 species (such as tartronate, mesoxalate, glycerate and lactate) to C_2 species (like oxalate and glycolate) occurred. It was reported the selectivity of oxalate and glycolate was higher on $PdAg_3$/CNT catalyst (39.2% oxalate and 37.9% glycolate) than PdAg/CNT catalyst (35.9% oxalate and 20.9% glycolate). Remarkably, the mechanism pathway was elucidated by using glycerate and mesoxalate intermediates as starting materials in the electrochemical process. Oxalate (91.8%) and formate (8.2%) were formed from mesoxalate intermediate while tartronate (53.0%) and oxalate (47%) were generated from electro-oxidation of glycerate (Benipal et al., 2017). Unlike these studies (PdAg and AuAg electrodes), three-dimensional (3D) nanoporous PtAg electrode favored DHA formation of mechanism pathway with the highest current density (7.5 mA cm^{-2}) and 15.4 times higher than the commercial Pt/C catalyst. The remarkable DHA selectivity of 82.6%, 61.5%, 79.2% and 79.8% were obtained at applied potentials of 0.7, 0.9, 1.0 and 1.3 V vs. RHE, which are 1.64, 1.46, 2.10 and 2.12 times those of the Pt/C electrocatalysts, respectively (Zhou et al., 2019b). Its interconnected porous structure is advantageous for the glycerol, intermediates and products diffusion (Fu et al., 2016) as well as to prevent their accumulation on catalysts surface, hence enhancing its stability (Zhang et al., 2015).

Pt catalyst could also be fortified by incorporating support like graphene, carbon black, carbon nanocubes, multi-walled carbon nanotube (MWCNT), etc. The morphology of the graphene nanosheets could be created as wrinkles surface, thus, it will generate a large surface area with powerful adsorptive sites for glycerol electro-oxidation reaction (Wang et al., 2016a). This fortification will benefit in reducing the amounts of metal loading, as well as enhancing their stability, electrocatalytic activity, and utilization efficiency. As such, Lee et al. (2019b) attained 1.6 fold higher peak current density of highly dispersed Pt nanoclusters supported on microporous three-dimensional (3D) graphene-like carbon (Pt/3D GLC) than conventional Pt/C which relatively less poisoned by accretion of intermediates on its surface compared to Pt/C. Their reaction kinetics study using Tafel slopes revealed a value of 171.28 mV/dec was obtained on Pt/3D GLC while Pt/C has 201.83 mV/dec value. It indicates faster electrocatalytic reaction kinetics was achieved at lower Tafel slope value that shows Pt/3D GLC leads to enhanced glycerol electro-oxidation reaction (Lee et al., 2019b). Zhou et al. (2018) developed a few hybrid catalysts comprising Pt particles incorporated on graphene nanosheet (GNS) and fortified with ruthenium (Ru), nickel (Ni) and rhodium (Rh). Among the catalysts, they found PtRhNi/GNS and PtRh/GNS catalysts unveil the superior activity in terms of the largest current density (5.58 and 4.47 mA cm^{-2}, respectively) and lowest onset potential (-0.71 and -0.719 V vs. SCE, respectively) toward glycerol electro-oxidation, which due to their synergistic effects. It's worthy to mention that the introduction of Ru on PtRuNi/GNS catalyst has facilitated C–C bond of glycerol to glyceraldehyde better as the selectivity of this intermediate was higher (39.2%) than the bi-metallic PtNi/GNS catalyst (29.8%) at 0.2 V vs. SCE. Kim et al. (2017b) found after 500 cycles of CV analysis, Pt_5Ru_5/C catalyst has higher stability with a normalized current density ratio of 0.635 than the conventional Pt/C catalyst (0.465). The remarkable performance of this catalyst is traceable to the DHA formation on Pt_5Ru_5/C catalyst with 35% selectivity in 0.5 M H_2SO_4 medium.

As nickel has the ability to provide different oxygen-containing species such as NiOOH and $Ni(OH)_2$ through electrodeposition, predominantly in alkaline electrolyte, Han et al. (2017) and Moraes et al. (2019) have prepared ALD(TiO_2)-Ni/C and Pt-NiO/Ti electrocatalysts by atomic layer deposition (ALD) and thermal decomposition of polymeric precursors, respectively. The addition of nickel element on electrocatalysts would yield DHA intermediate. TiO_2 was coated on Ni/C and this layer has enhanced the surface oxidation state of nickel without significant loss of active surface sites, consequently leading to the formation of more abundant metal oxyhydroxides ($Ni(OH)_2$) as the active sites for the glycerol electro-oxidation reaction (Han et al., 2017). They revealed ALD(TiO_2)-Ni/C electrocatalyst displays high activity with 2.4 times of current density higher than the uncoated Ni/C. The onset potential of glycerol oxidation with ALD(TiO_2)-Ni/C occurred at a more negative value compared with the Ni/C catalyst, indicating an improvement in oxidation kinetics. As studied by Moraes et al. (2019), a high catalytic activity of Pt-based incorporated with nickel also could be observed on $Pt_{0.8}Ni_{0.2}O_y$/Ti and $Pt_{0.9}Ni_{0.1}O_y$/Ti electrocatalysts. They have better electrical conductivity compared to NiO/Ti and PtO_y/Ti catalysts due to proton transfer redox processes with O/OH ligands on the Ni atoms in alkaline medium and hence, it will increase the kinetics of glycerol electro-oxidation. Also, the voltammetric charge was increased because of their synergistic effects with a porous and high active surface area. The surface area was increased as the Pt content increased, but, only up to $Pt_{0.8}Ni_{0.2}O_y$/Ti (706.2 cm^2). Higher Pt content ($Pt_{0.9}Ni_{0.1}O_y$/Ti) has reduced its surface area (307.1 cm^2) because the layer became more compact and dense, leading to reducing the porous grains and hence, decrease the voltammetric charge (Moraes et al., 2019).

Several authors have also reported the significant performance of Pt catalysts combined with the p-group elements. Simões et al. (2011) modified carbon-supported Pd- and Pt-based nanoparticles by depositing the low amount of bismuth (Bi) on their surfaces (Simões et al., 2011). The modification of noble metals electrodes with foreign metals will influence the amount and composition of adsorbed species (González-Cobos et al., 2016). This modification improved the glycerol electro-oxidation activity when the different composition of noble catalysts (Pt and Pd) and co-catalyst (Bi) were applied. $Pd_{0.45}Pt_{0.45}Bi_{0.1}$/C successfully traded the expensive Pt into half and performed better than monometallic metals like Pt/C and Pd/C electrodes. There seems to be the same general agreement by Coutanceau et al. (2014) on

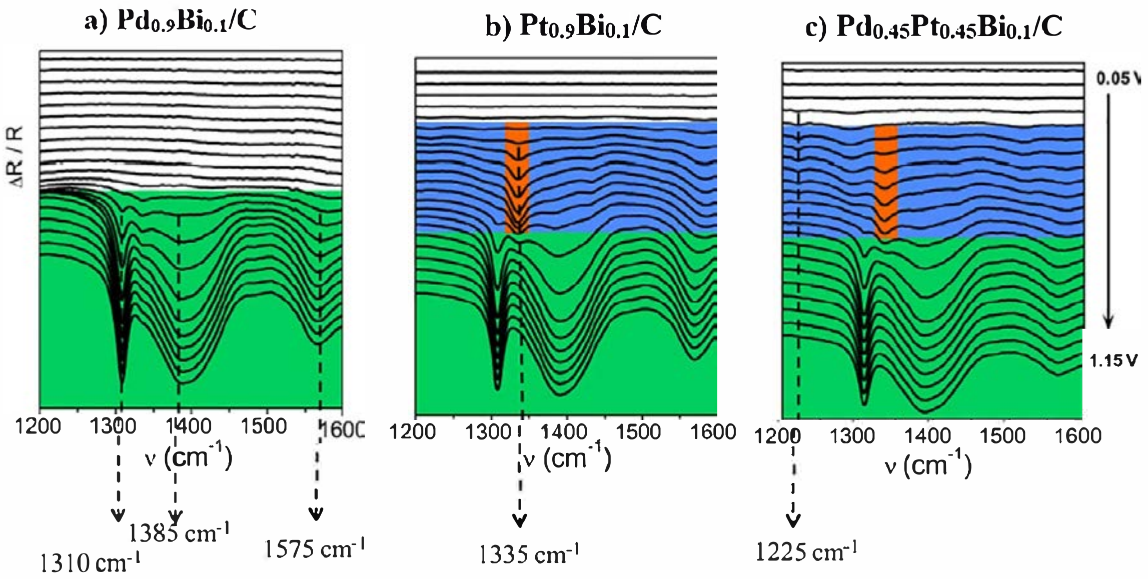


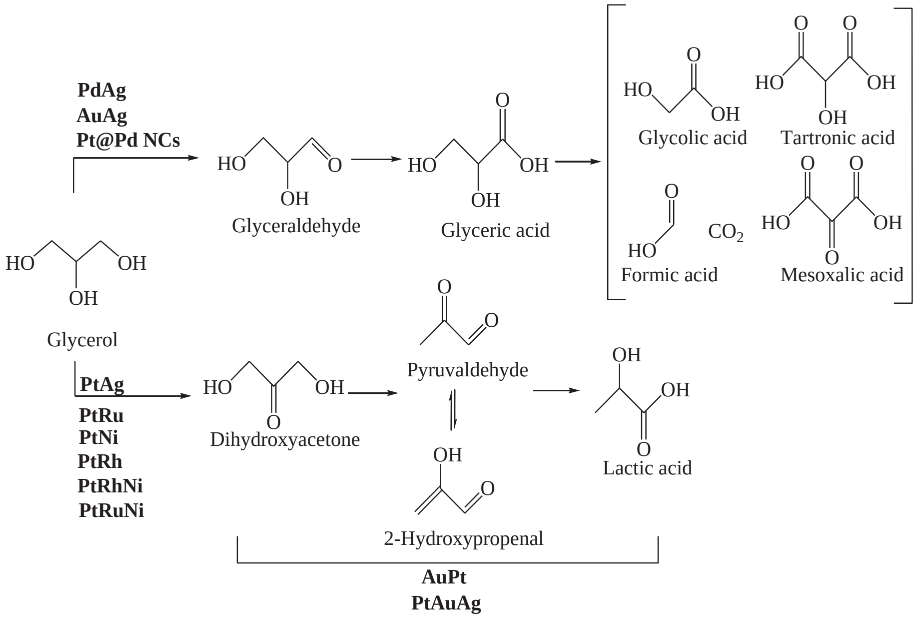
Fig. 2. Infrared spectra recorded on different catalysts; a) $Pd_{0.9}Bi_{0.1}/C$ b) $Pt_{0.9}Bi_{0.1}/C$ and c) $Pd_{0.45}Pt_{0.45}Bi_{0.1}/C$ in 0.1 M of glycerol and 1.0 M of NaOH at 20 °C (Coutanceau et al., 2014).

this issue when glycerol electro oxidation on Pt_9Bi_1/C and $Pd_{0.45}Pt_{0.45}Bi_1/C$ electrodes were started at lower onset potential 0.2 V vs. RHE. The modification of Pd electrode by bismuth did not affect the products selectivity. Carboxylate compounds were only formed on $Pd_xBi_{10\ x}/C$ electrode at too high applied potential. But, aldehydic and ketonic compounds with high selectivity were obtained on Pt electrode containing bismuth at very low potentials as demonstrated in Fig. 2. This is because the glycerol oxidation occurred without activation of OH species at potentials and thus, led to the formation of aldehyde (absorption band at ca. 1335 cm ^{1}) and ketone (absorption band at ca. 1225 cm ^{1}) groups instead of carboxylate group (Coutanceau et al., 2014).

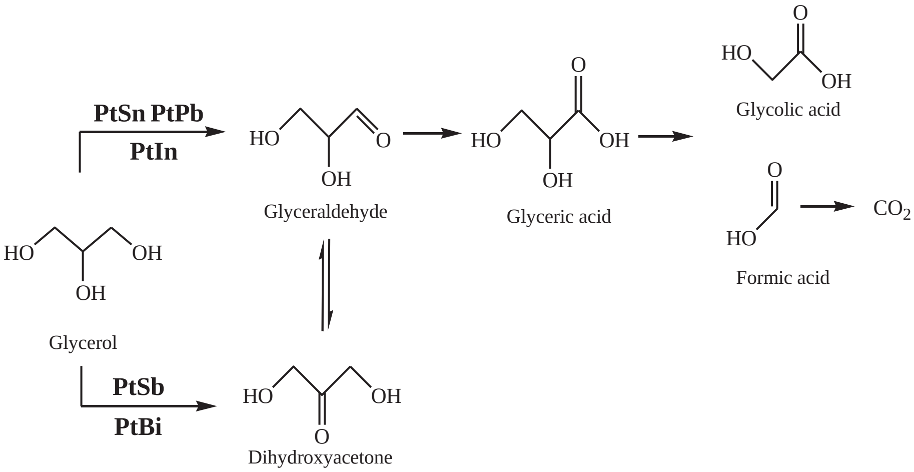
In a similar study conducted by Kwon et al. (2014), the enhanced catalytic activity and selectivity towards dihydroxyacetone (DHA) using carbon supported Pt/C with adatoms (Sb, Bi, Pb, Sn and In) were also recognized. Both Bi and Sb promoted the secondary hydroxyl oxidation to DHA while primary hydroxyl oxidation was favored by Pb, In and Sn elements. From the CV scan that has been conducted in 0.1 M glycerol with 0.5 M H_2SO_4, it was shown that the presence of irreversibly modified Sb on Pt/C had improved the glycerol electro oxidation and selectively oxidized the secondary hydroxyl group to DHA with the highest selectivity of DHA (80%) at 0.35 V vs. RHE (Kwon et al., 2014a), which is in agreement with recent results using PtSb/C by Lee et al. (2016). PtSb nanoparticles can enhance the oxidative dehydrogenation of glycerol and hinder further oxidation of intermediate. DHA intermediate was formed with 61.4% yield and 90.3% glycerol conversion at 0.797 vs. SHE (Lee et al., 2016). The selectivity of nearly 100% DHA from glycerol also could be achieved successfully when Pt/C with Bi was used as the electrode (Kwon et al., 2012). The presence of Bi in the electrode is capable to block primary hydroxyl oxidation, avoid CO formation and offers specific Pt Bi surface site for secondary hydroxyl oxidation and led to DHA formation. The glycerol electro oxidation on PtBi electrode was predominantly generated DHA intermediate which is contradicting to pure Pt catalyst that formed glyceraldehyde as main intermediate. However, the improvement of activity and selectivity towards DHA which is due to the bismuth addition is only applicable for Pt(1 1 1) electrode but not on Pt(1 0 0) electrode (Garcia et al., 2017a). With a combination of detailed electrochemical experiments, online spectroscopy and density functional theory (DFT) calculations, Garcia et al. (2016) proved that the surface crystallographic structure of Pt(1 1 1) and Pt(1 0 0) catalysts will affect the activity and selectivity of desired products in acidic medium. This is due to the different binding modes of dehydrogenated glycerol to their surfaces at the initial of oxidation reaction. Based on the DFT study, on the Pt (1 0 0) electrode, enediol intermediate was formed when dehydrogenated glycerol bound through a double Pt = C bond (Garcia et al., 2016). Hence, only glyceraldehyde was formed as the stable intermediate via primary hydroxyl oxidation. But, on the Pt(1 1 1) electrode, dehydrogenated glycerol bound to the surface via two single Pt C bonds resulting in enediol intermediate which is subsequently favored both glyceraldehyde and dihydroxyacetone formation. Plus, from the stripping experiments, it was suggested that an inactive intermediate was strongly bonded during glycerol, glyceraldehyde and dihydroxyacetone oxidations, and it is very difficult to oxidize. The substitution of d group and p group elements on Pt catalyst is capable of significantly reducing electrode preparation cost and sustains the electrochemical conversion performance in future. Although it is obvious that further investigations are needed to determine both the mechanism of glycerol electro oxidation and electro reduction on platinum surface, general mechanism pathways on Pt based with d group and p group are suggested in Scheme 2 and Scheme 3, respectively.

4.2. pH of electrolyte

An electrolyte in the electrochemical conversion process is usually a salt that provides ions to enhance the conductivity of the solution (Frontana Uribe et al., 2010). The choice of electrolyte for different electrodes is important to selectively produce the desired intermediates for further reactions. Table 3 shows the merits and demerits of various electrodes in the alkaline or acidic medium, where this would be useful for future works in the selection of electrolyte based on the electrode types. With the increment of pH, the glycerol conversion rates changed which is due to the different conversion mechanisms in the presence of H^+ and OH concentrations. In acidic medium, Pt based catalyst demonstrates a better performance compared to alkaline medium where in particular, glyceraldehyde and DHA are obtained as intermediates, while, glyceric acid, tartronic acid, glycolic acid, glycoxylic acid, formic acid and CO_2 are formed as products from the glycerol electro



Scheme 2. General reaction pathway of glycerol electro-oxidation on Pt-based electrodes incorporated with d-group metals in alkaline medium.



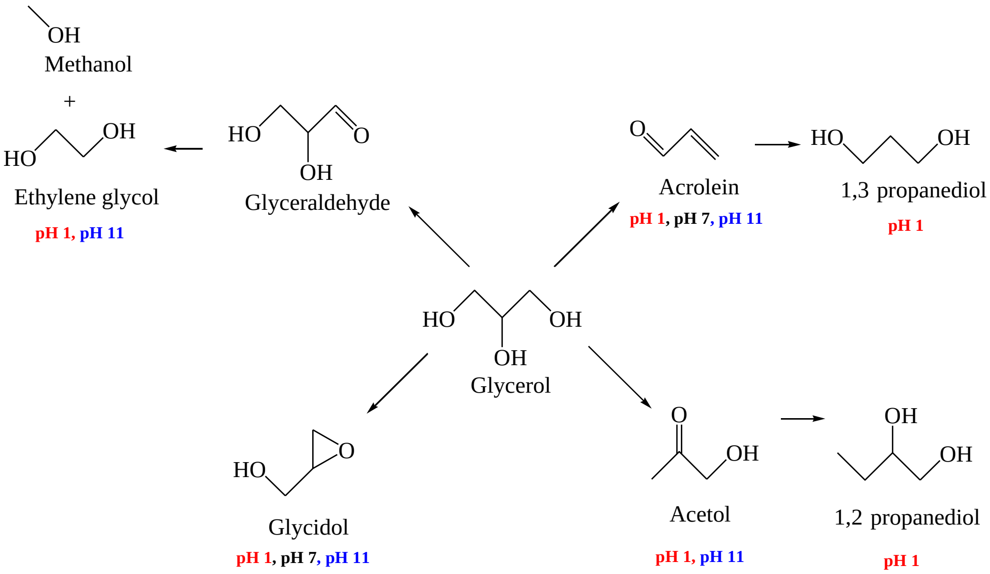
Scheme 3. General reaction pathway of glycerol electro-oxidation on Pt-based electrodes incorporated with p-group metals in acidic medium.

oxidation (Gomes and Tremiliosi Filho, 2011; Kongjao et al., 2011; Kwon et al., 2011b; Gomes et al., 2012).

The study on glycerol electro reduction reaction was started by Kongjao et al. (2011) but the influence of the initial solution pH (1, 7 and 11) for this reaction was done by Hunsom and Saila (2013). Following 13 h of electrolysis, Pt catalyst has shown its ability to break the C C bond to C_3 and C_2 species. The most elevated glycerol conversion rate was acquired at pH 1 (100%), followed by pH 11 (67.6%) and pH 7 (49.4%) (Hunsom and Saila, 2013). This is because the compounds were generated in higher amounts under strong acidic and alkaline media compared to a neutral medium. As shown in Scheme 4, ethylene glycol was only produced at pH 1 and 11 via dehydrogenation of glycerol to glyceraldehyde followed by the splitting of C C bond. Plus, in these media, acetol was formed through dehydration of primary hydroxyl group of glycerol. However, under a strong acidic condition (pH 1), only 1,2 propanediol and 1,3 propanediol were generated by the reduction of acetol and acrolein, respectively. The first order model was used to analyze the adsorption kinetics of glycerol electro reduction reaction and all pH are fitted with this model. It was noted that glycerol conversion rate was increased due to the high amount of products generated in the process but the mechanistic pathways of each pH reaction medium on Pt cathode catalysts have not been proved by the researchers. Hunsom and Saila (2015) carried further investigation by utilizing enriched glycerol on Pt electrode to explore the influence of initial pH (1, 7 and 11) towards the electrochemical conversion. According to the polarization curves (Fig. 3), it was proven that various peaks were obtained at pH 1 which was specified as the best condition for enriched glycerol conversion reactions with the highest current densities compared to the neutral and alkaline conditions (Hunsom and Saila, 2015). Though glycerol electro reduction mechanism pathway study is very limited, this reaction preferred acidic medium to produce acetol intermediate via dehydration which important for 1,2 propanediol formation (Ishiyama et al., 2013; Lee et al., 2018). From the recent catalytic studies, tungstic acid (H_2WO_4) has a potential role as the medium to reduce glycerol into propanediol

Table 3
Advantages and disadvantages of some of recent mono-metallic electrocatalysts/ electrodes.

Electrodes	Advantages	Disadvantages	References
Pt-based	■ The most active catalyst in fuel cell and electrolysis cell under acidic and alkaline conditions.	■ Expensive. ■ Easily poisoned by carbonaceous intermediates species such as CO that released from glyceraldehyde formation. ■ Lower catalytic activity in alkaline and neutral media compared to acidic medium.	(Kwon et al., 2012; Garcia et al., 2017b; Jr. et al., 2017; Araujo et al., 2019; Lee et al., 2019b; Moraes et al., 2019)
Pd-based	■ Less expensive and better poison tolerant than Pt catalyst. ■ At least 50 times abundant that Pt catalyst.	■ The durability and tolerance to poison are required to enhance.	(Ferreira et al., 2013; Coutanceau et al., 2014; Geraldes et al., 2015; Inoue et al., 2018)
Au-based	■ Less expensive than Pt and Pd catalysts. ■ Enhanced oxygen resistant and high tolerance to carbonaceous intermediates species. ■ Promotes C–C breakage to C_2 and C_1 products with higher overpotential than Pt catalyst.	■ Highly active under basic conditions.	(Kwon et al., 2011b; Kwon et al., 2014b; Qi et al., 2014; Dodekatos et al., 2018)
Ag-based	■ Less expensive than Pt and Pd catalysts. ■ Suitable as co-catalyst in Pt, Au and Pd catalysts since it helps facilitate C–C bond cleavage.	■ Weak performance, oxidation reaction is blocked at potentials > 1.125 V, irrespective of glycerol concentration in the solution.	(Hirasawa et al., 2013; Gomes et al., 2014; Suzuki et al., 2016)
Ni-based	■ Inexpensive and durable in alkaline medium as well as well-tolerant to poisoning. ■ Notable catalytic activity as Pt catalyst. ■ Ni has ability to provide different oxygen-containing species such as NiOOH and $Ni(OH)_2$, hence, improve adsorption/desorption of glycerol, intermediates and products when applied as co-catalyst.	■ Only active in alkaline medium. ■ Under acidic condition, the dissolution of nickel could be happened.	(Han et al., 2017; Lin et al., 2017; Moraes et al., 2019)



Scheme 4. Proposed reaction mechanism of glycerol electro-reduction on Pt cathode electrode in different pH of reaction media, as indicated (Hunsom and Saila, 2015).

compounds, which can be beneficial for 1,3 propanediol formation using the electro reduction reaction (Nakagawa et al., 2014).

The selectivity towards intermediates and final products from glycerol electro oxidation as well as the electrocatalysts (or electrodes) activity are strongly dependent on the pH of reaction media. Othman and Ahmad (2015) conducted glycerol electro oxidation on the gold plate (Au) and gold composite electrodes (Au PVC) using potassium hydroxide (KOH) and sulfuric acid (H_2SO_4) as the media. The glycerol electro oxidation rate occurred twice as much in alkaline medium on both Au and Au PVC electrodes compared to an acidic medium in which oxidation only happened once on Au electrode (Othman and Ahmad, 2015). However, more recently, Valter et al. (2018) proposed that Au electrodes also exhibited catalytic activity in acidic medium. Instead of using 0.5 M H_2SO_4 (Beden et al., 1987; Kwon et al., 2011a), they used 0.1 M $HClO_4$ as supporting electrolyte. Initially, both perchlorate ions and sulphate ions will compete with the relatively weakly bound electrically neutral glycerol for free adsorption sites. The stronger adsorption of sulphate ions than perchlorate ions on Au surface could be an explanation for the inactive catalytic activity of anode surface (Au catalyst) in 0.5 M H_2SO_4 medium previously. This is because the stronger binding of sulphate ions on Au surface has led to the blockage of its surface with the lack of observed activity. Computationally, it was observed the partial dehydrogenation started in the potential range below 1.0 V vs. RHE. The formation of dihydroxyacetone, 2,3 dihydroxy 2 propenal and glyceraldehyde was observed and proposed at 0.39, 0.39, and 0.60 V vs. RHE, respectively, whereas the complete dehydrogenation to carbon monoxide (CO) happened at 0.50 V vs. RHE (Valter et al., 2018). The presence of this CO specified that the C C bond was broken which means low selectivity in C_3 species in the process. Because of the adsorbed CO and glyceraldehyde on the sur

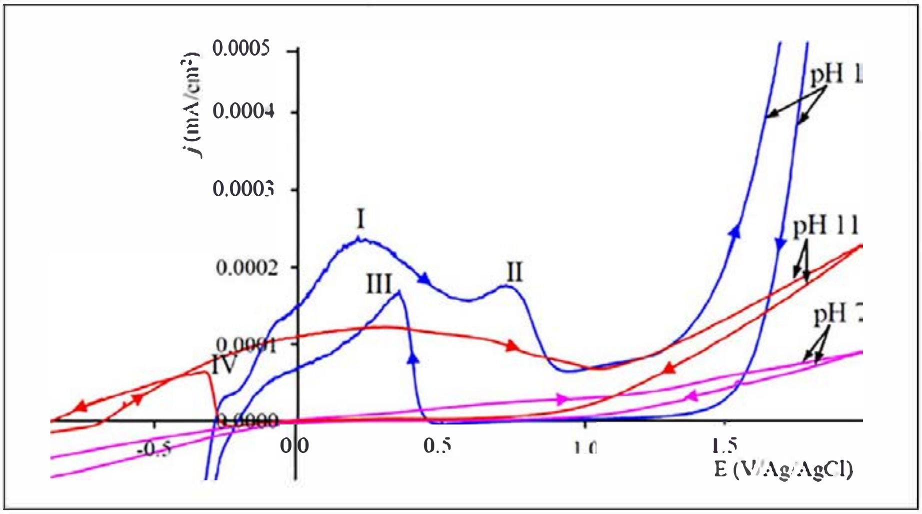


Fig. 3. Cyclic voltammetery curve of 0.3 M enriched crude glycerol at three different pH values using a Pt electrode (Hunsom and Saila, 2015).

face has led to very low activity and current densities in their CV curve.

Yet, Au and Au based electrodes still show higher activity in the alkaline medium compared to the acidic solution. It also has well tolerant to adsorbed species poisoning species such as CO where this species is the main poisoning agent for Pt and Pd catalysts. Zhang et al. (2012a) evaluated the reactivity of glycerol, methanol and ethylene glycol in an AEM direct glycerol fuel cell (AEM DGFC). From the CV curves, the results revealed that glycerol has higher catalyst activity on Au/C with lower on set potential and higher electro oxidation currents compared to ethylene glycol and methanol. Since the first deprotonation of H_α in alcohol on Au/C involved base catalyzed, a lower pK_a will favour the higher reactivity. To clarify, glycerol with pK_a of 14.15 is easier to deprotonate into highly reactive glyceroalate in high pH media compared to ethylene glycol (14.77) and methanol (15.50). The higher pH will boost the OH adsorbed coverage rate on the Au/C surface and enhance glycerol electro oxidation. However, when the concentration of KOH was too high (3.0 M), the excessive $OH_{adsorbed}$ on the Au catalyst surface blocked the glycerol adsorption, resulting in a lower reactivity (Zhang et al., 2012a). De Souza et al. (2017) further compared the glycerol electro oxidation with other 3 carbon atoms chain alcohols such as 1 propanol, 2 propanol, propane 1,2 diol and propane 1,3 diol on Au catalyst in 1.0 M NaOH medium. Glycerol showed the highest reactivity followed by propane 1,2 diol, where both exhibited high C C bond cleavage rate with the presence of C_1 and C_2 species. The vicinal OH groups in glycerol and propane 1,2 diol is a key component to stimulate the C C breaking of molecules and enhance the electro oxidation reaction in alkaline medium. The current densities were higher in the alkaline medium compared in the acidic and neutral media. It was reported that the surface was blocked with ClO_4^- and inhibited the electro oxidation in the acidic and neutral media. Additionally, the lack of alkoxide ions or active species in the alkaline medium could negatively affect the oxidation rates of the investigated 3 carbon atom chain alcohols. Under acidic condition, the alcohol molecule is protonated by H^+ rather than deprotonated H^+ of alcohol molecule (losing H^+) to form alkoxide. The repulsive forces between the positively charged of alcohol molecule and gold electrode will exist and thus, the adsorption process of alcohol molecule to the surface will be difficult to achieve. However, the unprotonated alcohol adsorbed on surface via Brownian motion occur but the quantity of active species to electrode surface is not sufficient to proceed more oxidation reaction, which resulting low current densities (De Souza et al., 2017).

As mentioned in the electrodes materials section, Pt electrodes containing bismuth in acidic solution have the potential to produce dihydroxyacetone (DHA) intermediate (Kwon et al., 2012). Nonetheless, DHA also could be formed in alkaline medium with the presence of bismuth on Pd electrode (Zalineeva et al., 2015). Other than the presence of bismuth which inhibits the dissociative adsorption/oxidation of primary OH to glyceraldehyde, DHA formation also could be explained by the Lobry de Bruyn van Ekenstein transformation (Epimerization) or known as rearrangement reaction of the equilibrium aldose and ketose. This rearrangement happens in the base catalyzed reaction and thus, when the local pH increased, the reaction favoured the labile OH group adsorption and further formation of very reactive alcoholate (CH_2OH CHO CH_2OH). This species was further transformed into DHA intermediate (Clavilier et al., 1988; Zalineeva et al., 2013). The Lobry de Bruyn van Ekenstein transformation also can be applied in an acidic medium which well known as aldose ketose transformation and tautomeric enediol as intermediate (Nimlos et al., 2006; Garcia et al., 2016). But, these Pd based electrocatalysts are still highly active under alkaline medium compared to the acidic medium. For instance, Pd_3Sn/phen C has superior durability and poisoning tolerance in 0.1 M KOH higher than Pd/C (Wang et al., 2016b). Since nickel and silver also are very stable in alkaline medium, the utilization of these elements on Pd catalyst (PdNi/C and PdAg/C) in 0.1 M NaOH has exhibited good reaction kinetics at low applied potentials (Holade et al., 2013b). The CO poisoning that owns by Pd catalyst was successfully reduced by a bifunctional mechanism of the oxidative desorption involving the transfer of OH species at lower potentials from the $Ni(OH)_2$ surface toward adsorbed organic molecules close to the palladium surface where the reaction takes place (Holade et al., 2013a). For Ag element, according to the d band theory, the d band of Pd catalyst was shifted when Ag was added on its surface, leading to more hydroxyl groups adsorbed on PdAg/C and subsequently, enhanced the removal of CO from PdAg/C surface (Zhang et al., 2017).

In Ferreira et al. (2013) work, carbonate was generated during glycolate and oxalate formation during glycerol electro oxidation in 0.1 M KOH. But, when low pH or OH concentrations (0.1 M KOH) are used, carbonate was abruptly substituted to a mechanism route that generates CO_2 at high potentials. The formation of CO_2 instead of CO is significant as demonstrated by Gomes et al. (2013). The results exposed the effect of glycerol concentrations (0.05 M, 0.1 M, 0.5 M, and 1.0 M) in an acidic medium towards the glycerol adsorption and electro oxidation pathways. At high glycerol concentration, the Pt surface was more covered glycerol

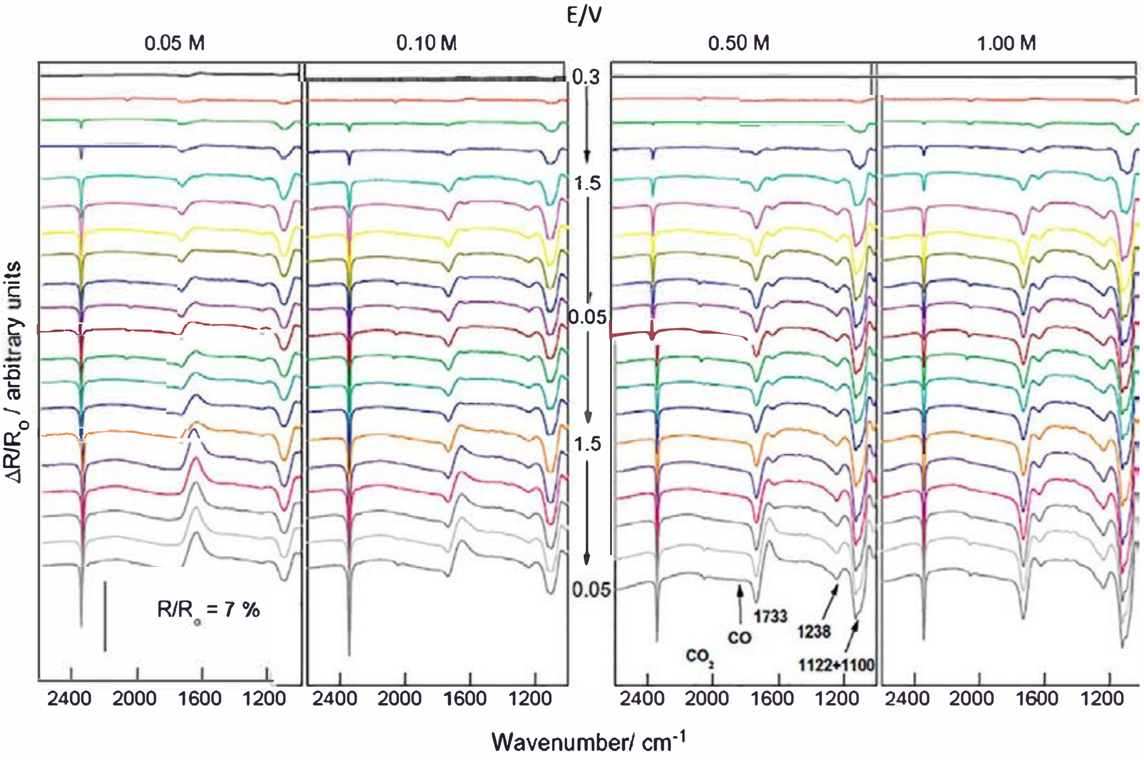


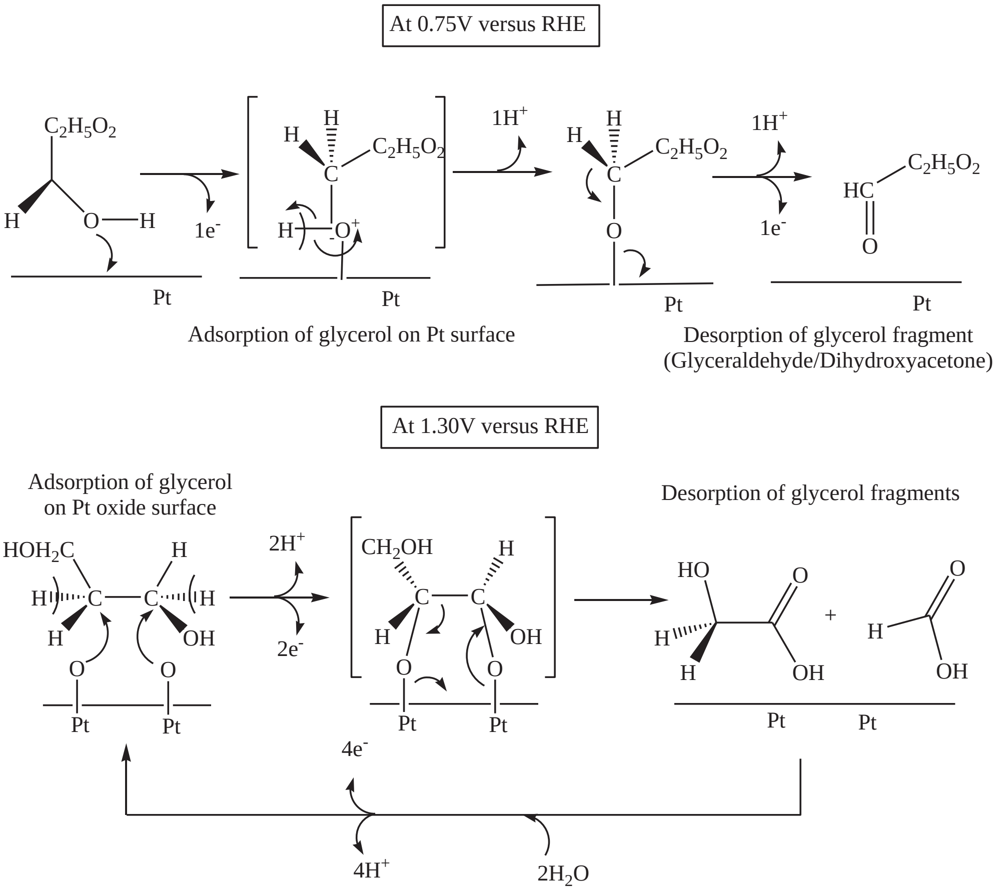
Fig. 4. In situ FTIR spectra for a Pt electrode in 0.1 M $HClO_4$ and different concentrations of glycerol (Gomes et al. 2013).

adsorbed residue and thus, inhibited the water co adsorption. The formation of adsorbed OH species on the Pt surface was delayed and further the CO_{ads} desorption into CO_2 as defined from Langmuir Hinshelwood mechanism cannot be happened; (CO_{ads} + OH_{ads} → CO_2 + H^+ + e). Consequently, CO remains adsorbed on Pt up to higher potentials and led to catalyst poisoning. The formation of the CO layer was also contributed from the glycerol oxidation to glyceraldehyde in the concentrated glycerol medium at the low and medium potential. In diluted glycerol, CO_2 was successfully formed 2343 cm ^{1} from CO and carboxylic acids generation seems to be independent on the glycerol concentration for this contribution. This is because CO_2 was partially oxidized from carboxylic acids at high potential (2040 cm ^{1}) as shown in in situ FTIR spectra (Fig. 4) (Gomes et al., 2013).

Though the removal of CO species and high desired products selectivity could be achieved in several current studies, the low yield of these products remained as one of the main issues. As such, under strong acidic conditions cleavage of glycerol is the main anodic reaction and the current yield is low, thus, the utilization of alkali hydroxides will provide better current yield. But large excess is needed as alkali hydroxides are consumed by many competitive reactions leading to complex product mixtures. To encounter this problem, Lux et al. (2010) have used alkali metal salts under acidic or alkaline medium because mixtures of metal ions will accelerate the rate determining step. In their work, with 3.6% (w/w) $Al_2(SO_4)_3$ medium, lactic acid with 90% yield was successfully formed and this remarkable yield hasn't achieved by other work. Angelucci et al. (2013) studied the interaction of hydrated alkali metal cations ($M^+(H_2O)_x$, M^+ = Li^+, Na^+ and K^+) with $OH_{adsorbed}$ on Pt catalyst and found that the current density of glycerol electro oxidation reaction increased with increasing cations radius (Li^+ < Na^+ < K^+). This happened due to the formation of clusters resulting from non covalent interactions between hydrated cations and $OH_{adsorbed}$ on Pt, which is favored as the cation radius decreased. In Li^+ electrolyte, OH_{ad} $Li^+(H_2O)_x$ clusters partially blocked the Pt surface and inhibited the reaction to occur, leading to low current density. The choice of suitable electrolyte is vital in achieving high catalytic activity as well as products selectivity and yield. The formation of CO species is not only hindered by using Au based, Ag based or Ni based electrocatalysts, but it also could be avoided by using the right concentrations of electrolyte and glycerol. As presented in Table 2, 0.5 M glycerol and 0.5 M electrolyte were mostly used to achieve high selectivity of products. A high concentration of glycerol only could be used on Au based electrodes since it has the ability to oxidize and remove adsorbed CO species from its surface efficiently. To avoid low catalytic activity, the electrolyte with high cations radius like NaOH and KOH should be used.

4.3. Applied potential and current density

Fundamentally, electrochemical conversion could be conducted on the current (galvanostatic) or applied potential (potentiostatic) is controlled. Both parameters have high impacts especially on the selectivity of compounds formed during the process. In a potentiostatic mode, the desired molecular transformations can be determined accurately by only adjusting the applied potential. However, the rate of electrolysis is not controlled directly because the applied potential needs to set to the specific value and current corresponds to the electrode reaction. Hence, this mode may take a longer time to control the applied potential (Pauwels, 2018). Even though this mode is inexpensive to be operated in the laboratories, it is still not practical for operation on the industrial scale. This is ascribed to the additional cost associated with a potentiostat that could operate at the current values needed in large scale transformations. Thus, the galvanostatic mode is the best choice since the setup is much simpler for large scale electrolysis. It only controls the electrical current that flows through the cell using a galvanostat or a DC power supply and this device is cheaper than a high current potentiostat (Frontana Uribe et al., 2010).

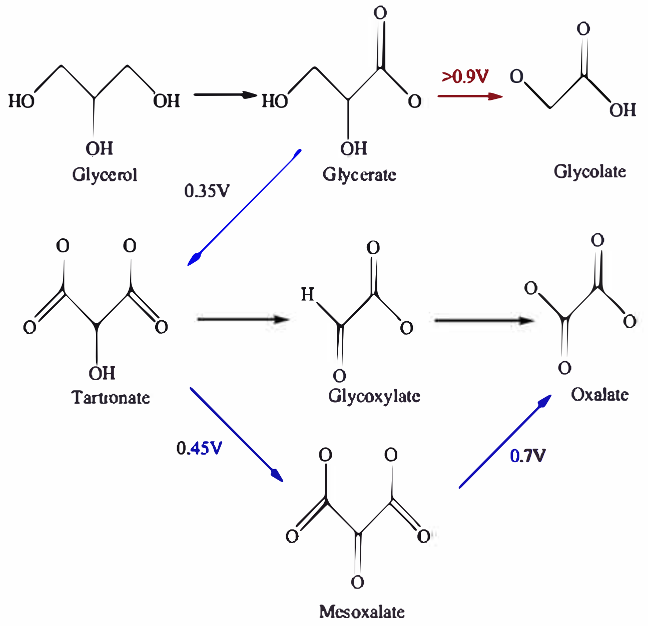


Scheme 5. Glycerol electro-oxidation pathway on platinum electrode in acidic medium at 0.75 V and 1.30 V versus RHE (Roquet et al., 1994.

In the potential electrolysis, glycerol is oxidized into the value added compounds the applied potential was set in the so called "oxygen region". A study showed the selectivity of glyceraldehyde intermediate is inversely proportional to applied potential (Roquet et al., 1994). In their work, the glycerol electro oxidation mechanism on the platinum electrodes has been explored in the acidic and alkaline media at the different applied potential. It has been proposed that the electro oxidation reaction involved different steps which are adsorption of hydroxyl (OH) group on the electrode surface, breaking inter atomic bonds, electronic charge transfer, interaction between oxygenated species on electrode surface (i. e.; adsorbed OH group or oxides) with fragments from glycerol molecule and desorption of reaction product (Gomes and Tremiliosi Filho, 2011). As demonstrated in Scheme 5, at 0.75 V vs. RHE, hydroxyl (OH) group from glycerol is adsorbed and interacted with the platinum electrode. In this regard, glycerol is oxidized into glyceraldehyde fragment. Meanwhile, at 1.30 V vs. RHE, glycerol interacted oxide formed on the Pt (PtO) electrode surface, led to the cleavage of C C bonds and produced glycolic and formic acids. The results also exposed 97% selectivity of glyceraldehyde was obtained at 0.75 V vs. RHE and was reduced to 56% selectivity at 1.30 V vs. RHE. The reduction in glyceraldehyde selectivity was agreed by Kim et al. (2014) as the applied potential increased, glycerol conversion was increased up to 97.3% at 1.297 V vs. SHE. Glyceraldehyde selectivity also changed when applied potential was tuned from 0.697 V (48.8% selectivity) to 1.097 V (2.5% selectivity) vs. SHE. Though glyceraldehyde selectivity was reduced at 1.097 V vs. SHE, glyceric acid selectivity has increased which indicates that acid was electro oxidized from glyceraldehyde intermediate (Kim et al., 2014).

With increasing of applied potential, it is said to be more C_3 and C_2 oxygenated compounds generated. Zhang et al. (2012b) produced high selectivity of glycolate using Au/C anode catalyst and Fe based cathode in the anion exchange membrane fuel cells. At 1.0 V vs. RHE, the glycolate selectivity was 41% and it was improved to 85% when the applied potential was adjusted to 1.6 V vs. RHE (2.0 M KOH with 1.0 M glycerol). Yet, when the applied potential was further increased, the selectivity of tartronate and glycoxylate were steadily decreased. In the continuation of their work, Zhang et al. (2014) studied the selectivity of tatronate and mesoxalate compounds using the same electrochemical system to verify their proposed mechanism. It was reported that when the anode potential was at <0.45 V vs. RHE, the major product was tartronate with the 79% selectivity and mesoxalate was not detected. Conversely, the selectivity of mesoxalate was increased gradually and reached the maximum selectivity of 57% with 26% selectivity of tartronate when the applied potential was increased to 0.69 V vs. RHE. The further increasing of the applied potential to 0.70 V vs. RHE showed the selectivity of mesoxalate was decreased to 55% and the selectivity of oxalate was increased from 5% to 8% which indicates the mesoxalate oxidation to oxalate. Scheme 6 summarizes and proves that the mechanism route of glycerol oxidation was shifted from glycolate to tartronate when the applied potential reduced from 0.9 V to 0.35 V vs. RHE (Zhang et al., 2014). It can be concluded that as the reaction takes place under mild conditions without any toxic or strongly oxidative reactants, it implies the regulation of the applied potential was able to control the products distribution and the mechanism pathways.

In the galvanostatic mode, Paula et al. (2014) produced hydrogen from the electrochemical glycerol reformation in alkaline



Scheme 6. Proposed reaction route for electro-oxidation of glycerol (Zhang et al., 2012b; Zhang et al., 2014).

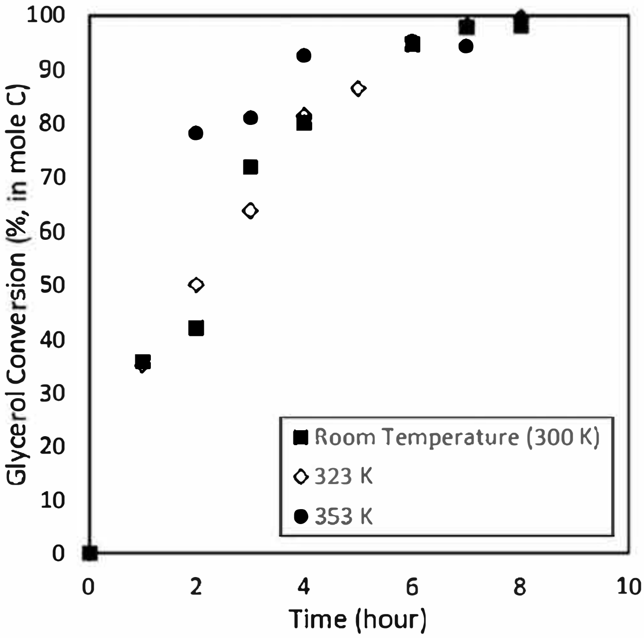


Fig. 5. Glycerol conversion from the electrochemical study at operating temperature from room temperature (300 K or 27 °C) to 353 K or 80 °C (Lee et al., 2019a).

doped polybenzimidazole proton exchange membrane (PBI based PEM) fuel cell (Paula et al., 2014). At high current density (0.80 A cm ^{2}) with a temperature of 60 °C, they successfully achieved the optimal hydrogen production and the result also demonstrated the highest selectivity of the oxidized compound was tratronate. Hunsom and Saila (2015) also proved the relationship of current densities with the selectivity of desired products using different current densities (0.08, 0.14, 0.24 and 0.27 A/cm^2) and Pt cathode at pH 1. They found acetol and 1,2 propanediol were produced only at medium to high current densities (0.14 0.27 A/cm^2) while acrolein and 1,3 propanediol were generated at current densities of 0.14 A/cm^2 and 0.24 A/cm^2. From this result, it indicated the dehydration of first hydroxyl group is not preferred at too low current density and second hydroxyl group is not preferred at too low or too high current densities. In addition, according to the Faraday's law, the increasing in the current density also led to the improvement of glycerol conversion which they have obtained the highest current density (0.27 A/cm^2) with ~100% glycerol conversion compared to 0.24 A/cm^2 with ~50% glycerol conversion after 8 h (Hunsom and Saila, 2015). However, too high a current density (0.27 A/cm^2) will not improve the generation of desired products because it will facilitate the glycerol decomposition to carbon dioxide (Ishiyama et al., 2013). Although the electrochemical conversion of glycerol with galvanostatic mode is limited, the regulation of this current would yield different product distribution, especially in the dehydration step. This step is important in the electro reduction of glycerol to selectively produce acetol or acrolein intermediate and subsequently reduced into 1,2 propanediol and 1,3 propanediol, respectively.

4.4. Reaction temperature

Glycerol electro oxidation or electro reduction is an endothermic reaction that requires electricity and a moderate amount of heat to drive the reaction. This phenomenon explains why glycerol conversion was low at room temperature and glycolic acid is a dominant product with high glycerol conversion at high temperature, as shown in Fig. 5. Glycerol is not completely electro oxidized to CO_2 at room temperature either in alkaline or acidic medium due to slow electro oxidation kinetics and high energy barrier of C C bond dissociation, but it can be obtained at around 250 °C (Ishiyama et al., 2013). When the temperature was increased, glycerol conversion rates increased and the conversion rates were 0.406 h ^{1}, 0.402 h ^{1} and 0.774 h ^{1} at 27 °C, 50 °C and 80 °C, respectively. The increasing of the temperature accelerates the C C bond breakage, hence, converting glycerol into glycolic acid with the highest yield of 66.1% and 72% selectivity at 80 °C on Pt catalyst (Lee et al., 2019a). It has promoted deeper glycerol electro oxidation similar to Jr. et al. (2017) work, indicating the glycerol electro oxidation process is thermally activated. They used two different temperatures (60 °C and 90 °C) to determine the influence of Pt loading on glycerol electro oxidation reaction and the result revealed that 90 °C of temperature favored C_3 species formation compared to the C_2 species like glycolate and oxalate. In a single direct alkaline fuel cell, 80 85 °C of temperature was identified as the optimum condition on Pd based, Pt based and Au based electrodes for this process (Geraldes et al., 2013; Zhang et al., 2013; Geraldes et al., 2015). Geraldes et al. (2015) obtained the highest power density at 85 °C on $Pd_{0.5}Au_{0.4}Sn_{0.1}/C$ (51 mW cm ^{2}), followed by $Pd_{0.5}Au_{0.1}Sn_{0.4}/C$ electrode with (42 mW cm ^{2}) while in a single alkaline direct ethanol fuel cell (ADEFC), 44 mW cm ^{2} was the best performance on $Pd_{0.9}Au_{0.1}$ electrocatalyst (Geraldes et al., 2013). Zhang et al. (2013) also reported the highest performances on Pt/C, Pd/C, and Au/C electrodes were achieved (184.2, 93.9 and 50.1 mW cm ^{2}, respectively) with 6.0 M KOH + 1.0 M crude glycerol at 80 °C compared to lower temperature of 60 °C. Above this temperature range (80 85 °C), membrane dryness and water management started to impede with electrode performance, which most likely because of an increase in cell resistance. The unstable performance of this glycerol electro oxidation reaction in fuel cells implied that a better reacting diffusion and higher kinetics of electrodes will be favored at higher temperatures.

The selection of these electrocatalysts or solid acid catalysts (additives) is critical in temperature studies because heat can deactivate thermally unstable catalysts. As such, a sulfonic acid resin (Amberlyst 15) is thermally unstable when operated around 120 °C and result in a sharp decrease in catalytic activity (Liao et al., 2009). The influence of temperature on reaction rates and activation energies could be determined by confirming experimental runs with various temperatures (i.e.; 235 260 °C) using the Arrhenius equation as presented in Eq. (4), where E_a (kJ/mol) is activation energy, R (J mol ^{1} K ^{1}) is the gas constant or the Boltzmann constant, K is the reaction rate constant, and A (s ^{1} for the first order reaction) is the frequency factor, which varies with the rate order and same unit as the rate constant. This equation shows the relationship between intrinsic temperature and equilibrium constant and hence, it can be used to determine rate law parameters. Based on this equation, when the temperature increases or activation energy decreases (when the catalyst is added), it will increase the rate constant that is directly proportional to the rate of reaction.

$$K \quad Ae^{E_aRT} \tag{4}$$

As shown in Fig. 6**a**, higher current densities were detected with the increased temperature, particularly at low and intermediate electrode potentials (120 500 mV). But, the current densities became almost equivalent at around 700 mV caused by high adsorbed OH coverage on Pt surface, which came from water dissociation at high applied potentials (Ishiyama et al., 2013). From the CV result (Fig. 6**a**), linearity between the natural logarithm of their current densities, ln i, and the inverse of reaction temperature was observed at electrode potentials of 150 500 mV as shown in Fig. 6**b**. Therefore, activation energy (E_a) for each electrode potential with different temperature could be calculated using Butler Volmer equations where Eq. (5) for anodic current (i) and Eq. (6) is represented for the apparent activation energy (E_a), where n is electron transfer, F is Faraday constant, A is pre exponential factor, α is transfer coefficient and R is gas constant. As demonstrated in Fig. 6**c**, the rate determining step of glycerol electro oxidation is proven to be dependent on temperature as well as electrode potential when the activation energy decreased (from 70 to 20 kJ mol ^{1}) with increasing electrode potential from 150 to 500 mV.

$$i \quad nFAexp\left(\frac{E_{a,0}}{RT}\right)exp\left(\frac{(1 \quad \alpha)nFE}{RT}\right) \tag{5}$$

$$E_a \quad R\left(\frac{\partial \ln i}{\partial\left(\frac{1}{T}\right)}\right)_E \quad E_{a,0} \quad (1 \quad \alpha)nFE \tag{6}$$

4.5. Additives

During the electrochemical process, redox catalysis can occur through direct electrolysis or indirect electrolysis (Fig. 7). Direct electrolysis only involved the transfer of heterogeneous electron between molecule substrate (i.e.; fuel) and electrode before or after chemical reaction while indirect electrolysis focused on a mediated electron transfer due to the addition of redox mediators or catalysts (i.e.; oxidizing agents or solid acid catalyst) in the electrolyte (Fuchigami et al., 2015). The use of electron mediators such as oxidizing agents can prevent the kinetic inhibition, electrode passivation and the over oxidation or reduction of the substrate which are associated with the direct electrolysis (Francke and Little, 2014; Pauwels, 2018). The presence of different additives in the

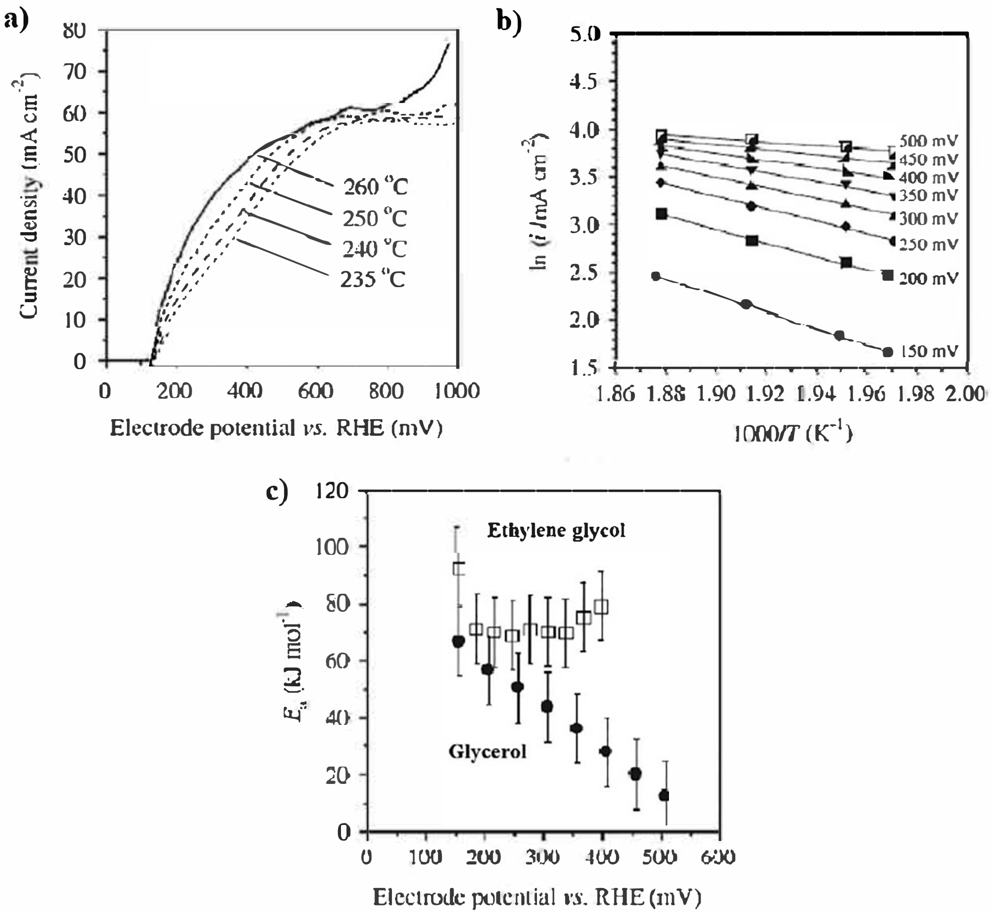


Fig. 6. a) Cyclic voltammogram of glycerol electro-oxidation on Pt/C at different temperatures (235-260 °C), b) Arrhenius plots for current densities of glycerol electro-oxidation at different applied potentials (150–500 mV) and c) Apparent activation energies of glycerol and ethylene glycol electro-oxidation vs. electrode potentials (Ishiyama et. al, 2013).

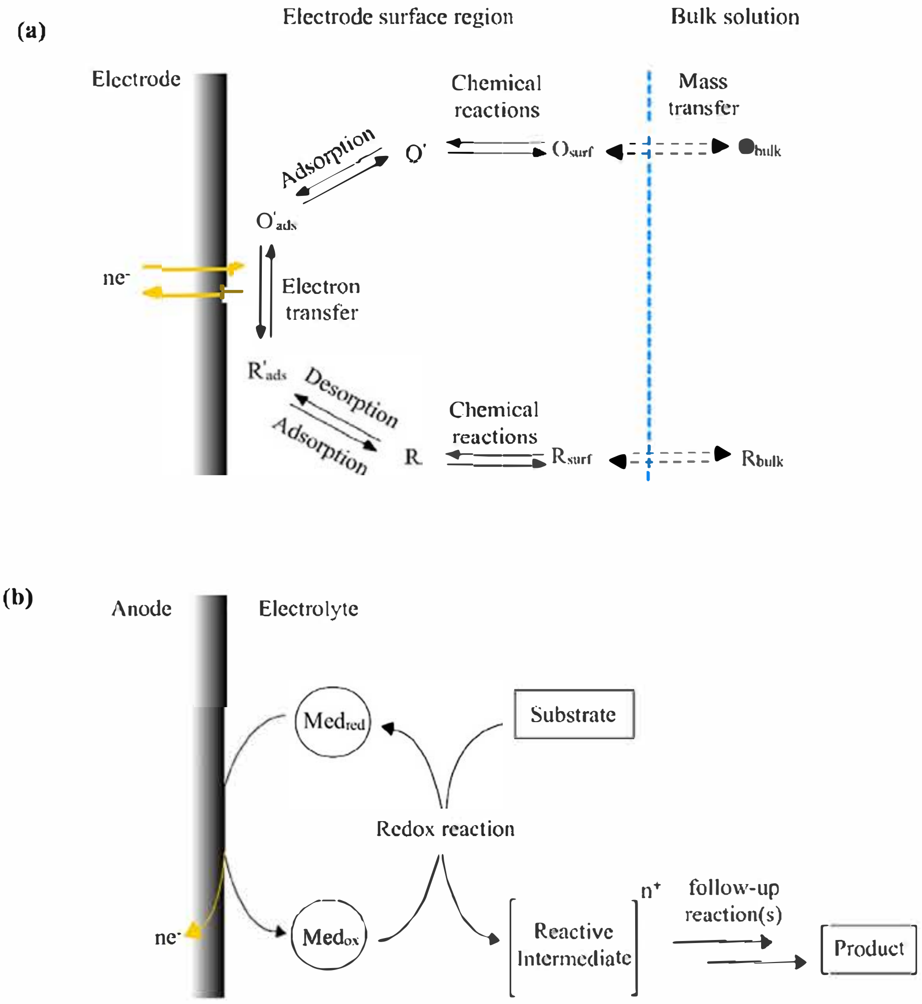


Fig. 7. Basic principles of a) direct electrolysis and b) indirect electrolysis (Francke and Little, 2014; Pauwels, 2018).

electrochemical conversion could improve the glycerol conversion and products distribution. To be noted, homogeneous mediators have been frequently used and Amberlyst 15 was the first heterogeneous catalyst that selectively dehydrated glycerol to acetol in Lee et al. (2018) work. After two years, Amberlyst 15 was used as additives with the different dosage in the glycerol electrochemical conversion to glycolic acid and lactic acid. When the catalysts dosage was varied from 6.4% to 9.6% w/v, the glycerol conversion rate increased from 0.635 to 0.724 h ^{1}, which showed the highest catalyst dosage has a faster kinetic reaction for this process. With 9.6% w/v Amberlyst 15, the glycolic acid selectivity and yield were up to 72% and 66%, respectively at temperature 80 °C. Under the same temperature, lactic acid achieved its highest selectivity (20.7%) and yield (18.6%) with 6.4% w/v Amberlyst 15 dosage. Since this study used the one pot electrochemical reactor, lactic acid may be formed through a direct electro reduction from pyruvic acid and glycolic acid obtained from direct glycerol electro oxidation (Lee et al., 2019a). It is important to know that the utilization of heterogeneous catalysts is capable to control product selectivity and has better separation from the obtained products (Nakagawa et al., 2018).

The earlier study obtained 1,3 dihyroxyacetone by applying 1.1 V vs. Ag/AgCl applied potential to a glycerol solution buffered at pH 9.1 in the presence of 15 mol % TEMPO (2,2,6,6 tetramethyl piperidine 1 oxyl) (Ciriminna et al., 2006). After 20 h, glycerol was selectively oxidized at secondary alcohol group which mediated by radical TEMPO to produce DHA (with 25% yield). When the time was prolonged to 200 h, the percentage yield of DHA was increased to 30% and hydroxypyruvic acid was formed with 35% yield (Ciriminna et al., 2006). Saila and co workers also attempted glycerol conversion on Pt cathode at pH 1 with different oxidizing agents (H_2O_2, $Na_2S_2O_8$ and TEMPO). In the absence of these oxidizing agents, glycidol and acrolein appeared as the primary products through dehydration and reduction. However, when these oxidants were added, each oxidizing agent successfully changed the direction of the mechanism path, principally via direct oxidation of primary or secondary hydroxyl group. As such, ethylene glycol, glycolic acid and 1,3 DHA were found as the main products in $Na_2S_2O_8$, H_2O_2 and TEMPO, correspondingly. Plus the conversion rate becomes faster from 14 h without oxidants to 10 h with oxidants (Saila and Hunsom, 2015). In Kwon et al. (2014b) work, glyceraldehyde intermediate also was not detected at the low applied potential in the presence of H_2O_2 oxidant. In alkaline medium, glycerol has no significant effect on the overall of glycerol electro oxidation activity or selectivity, nonetheless, the low activity can be seen under neutral and acidic conditions.

Recent efforts have focused on the deployment of the multi enzymes cascade to facilitate the complete electrochemical oxidation of glycerol to CO_2 (Hickey et al., 2014). With a combination of oxalate oxidase (OxO) and 4 amino TEMPO (TEMPO NH_2), one molecule of glycerol can be oxidized completely to CO_2 on the carbon electrode and deliberated 16 electrons. TEMPO NH_2 has exhibited the highest current density among other TEMPO derivatives and obtained an 8 fold increase in catalytic rate over the unmodi fied TEMPO. The results showed TEMPO NH_2 maintains the catalytic activity as low as pH 4 which allows OxO to function compared to the unmodified TEMPO that only active in the alkaline condition to pH 6. When TEMPO NH_2 was able to catalyze oxidation reaction at pH lower than its pKa, thus, it is assumed that the amine (NH_2) functional group is capable to lower the energy required for deprotonation/oxidation of the TEMPO NH_2 hydroxylamine intermediate. Glycerol cascade was initially oxidized to glyceraldehyde and further oxidized for multiple times to mesoxalic acid. A combined OxO and TEMPO NH_2 subsequently converted mesoxalic acid to glycoxylic acid, oxalic acid and finally to CO_2. This result differs from Saila and Hunsom (2015) that used the unmodified TEMPO and favoured secondary hydroxyl oxidation pathway. A larger amount of the nitrosonium cation from higher TEMPO concentration has increased the yield of 1,3 DHA from 57.2% to 69.2% with increasing concentration of TEMPO (from 1 to 5 mM TEMPO).

The presence of these additives either in homogeneous or heterogeneous form, in the electrochemical conversion, could selectively produce the desired intermediates and products from glycerol electro oxidation or reduction reaction. Table 4 presents the additives that have been used in the glycerol electrochemical conversion studies and several solid acid catalysts that were used in the glycerol catalytic conversion. These solid acid catalysts have potential to be applied as the acidic electrolyte in this process especially for dehydration step. Solid acid catalysts are much better than the mineral acids media like H_2SO_4, HCl and $HClO_4$ because these mineral acids require neutralization in the water quenching step at the end of the process, leading to the salt waste formation. With solid acid catalysts, they can be separated easily and reused several times without loss of activity in the process. The reactions are also generally clean and products will be obtained in high purity (Gupta and Paul, 2014).

Literature has shown that the combination of noble metal catalysts with solid acid catalysts yielded 1,2 propanediol and 1,3 propanediol as products of hydrogenolysis reaction, while propanols (1 PrOH and 2 PrOH) and propane were obtained from overhydrogenolysis reaction. However, propanols and propane have not been regarded as major targets in the glycerol conversion because they have lower market prices as well as poorer atom efficiency in their production compared to 1,2 propanediol and 1,3 propanediol. The addition of solid acids catalysts (such

Table 4
Additives (oxidants and solid acid catalysts) used in the glycerol electrochemical conversion and glycerol catalytic conversion.

Additives	Electrolyte	Reaction conditions	Products (selectivity (%))	Products (yield (%))	References
Glycerol electro-oxidation					
$Na_2S_2O_8$[a] (1 mM)	0.3 M glycerol + pH 1.0	A: Pt C: Pt CD: 0.14A/cm^2 25 °C 24 h 100%[d]	–	EG (63), GCA (5), GCD (25–30)	(Saila and Hunsom, 2015)
H_2O_2[a] (1 mM)	0.3 M glycerol + pH 1.0	A: Pt C: Pt CD: 0.14A/cm^2 25 °C 24 h 100%[d]	–	EG (20), GCA (21), GCD (20–22)	(Saila and Hunsom, 2015)
H_2O_2[a] (10 mM)	0.1 M glycerol + 0.1 M NaOH	A: Au C: Au E: 1.6 V vs RHE 25 °C	GLDA, GLA, FA, GA	GLDA, GLA, FA, GL	(Kwon et al., 2014b)
TEMPO[a] (1 mM)	0.3 M glycerol + pH 1.0	A: Pt C: Pt CD: 0.14A/cm^2 25 °C 24 h 100%[d]	–	EG (1–5), GCA (10–15), GCD (10–15), DHA (55), 1,2-PDO (1–3), ACT (1–3)	(Saila and Hunsom, 2015)
TEMPO[a] (3 mM)	0.3 M glycerol + pH 1.0	A: Pt C: Pt CD: 0.14A/cm^2 25 °C 24 h 100%[d]	–	EG (1–5), GCA (10–15), GCD (10–15), DHA (63–66), 1,2-PDO (1–3), ACT (1–3)	(Saila and Hunsom, 2015)
TEMPO[a] (5 mM)	0.3 M glycerol + pH 1.0	A: Pt C: Pt CD: 0.14A/cm^2 25 °C 24 h 100%[d]	–	EG (1–4), GCA (10–15), GCD (10–15), DHA (69.2), 1,2-PDO (1–2), ACT (1–2)	(Saila and Hunsom, 2015)
15% mol TEMPO (0.0075 M)[a]	0.05 M glycerol + 0.2 M bicarbonate (pH 9.1)	A: Glassy carbon C: Pt E: 1.1 V	DHA (25), HPA (35)	DHA (35), HPA	(Ciriminna et al., 2006)

Table 4 (*continued*)

Additives	Electrolyte	Reaction conditions	Products (selectivity (%))	Products (yield (%))	References
		vs. Ag/AgCl 25 °C 200 h 100%[d]			
Amberlyst-15[b]	0.3 M glycerol + 24 g Amberlyst-15	A: Pt C: CBAC Current: 2.0 A 80 °C 6 h 100%[d]	–	GA (66), LA (15–20), FA (5–19), EA (1–5), EG (1–5), AA (1–5)	(Lee et al., 2019a)
Glycerol electro-reduction					
9.6% (w/v) Amberlyst-15[b]	0.3 M glycerol + 24 g Amberlyst-15	A: Pt C: Pt Current: 2.0 A 80 °C 8 h 67%[d]	1,2-PDO (61), ACT (24), DEG (15)	–	(Lee et al., 2018)
9.6% (w/v) Amberlyst-15[b]	0.3 M glycerol + 24 g Amberlyst-15	A: Pt C: CBAC Current: 2.0 A 80 °C 8 h 74%[d]	1,2-PDO (86), ACT (3), DEG (11)	–	(Lee et al., 2018)
9.6% (w/v) Amberlyst-15[b]	0.3 M glycerol + 24 g Amberlyst-15	A: Pt C: CBD Current: 2.0 A 80 °C 8 h 88%[d]	1,2-PDO (68), ACT (17), DEG (15)	–	(Lee et al., 2018)

Additives	Glycerol/water/catalyst + additive (g)	Reaction conditions	Products (selectivity (%))	Products (yield (%))	References
Glycerol hydrogenolysis					
$H_3PW_{12}O_{40}/ZrO_2$ or TPA/ZrO_2 (15 wt%)[b]	10/40/0.15 + 0.3	Ru/C[c] 6 H_2/MPa 453 K 8 h 44.0%[d]	1,2-PDO (64.3), EG (27.0), Others (8.9)	–	(Balaraju et al., 2009)
Nb_2O_5[b]	10/40/0.15 + 0.3	Ru/C[c] 6 H_2/MPa 453 K 8 h 44.6%[d]	1,2-PDO (60.9), EG (21.1), Others (12.3)	–	(Balaraju et al., 2009)
Nb_2O_5[b]	10/40/0.6 + 1.2	Ru/C[c] 6 H_2/MPa 453 K 8 h 62.8%[d]	1,2-PDO (66.5), EG (21.2), Others (12.3)	–	(Balaraju et al., 2009)
Nb_2O_5[b]	10/40/0.45 + 0.9	Ru/C[c] 6 H_2/MPa 453 K 8 h 58.7%[d]	1,2-PDO (64.7), EG (29.1), Others (14.2)	–	(Balaraju et al., 2009)
Amberlyst-15[b]	4/16/0.15 + 0.3	Ru/C[c] 8 H_2/MPa 393 K 10 h 79.3%[d]	1,2-PDO (74.7), 1-PrOH (7.7), 2-PrOH (1.6), EG (6.8)	–	(Miyazawa et al., 2007a)
Amberlyst-70[b]	4/16/0.015 + 140 μmol H^+	Ru/C[c] 8 H_2/MPa 453 K 10 h 48.8%[d]	1,2-PDO (70.2), 1,3-PDO (1.3), 1-PrOH (7.1), 2-PrOH (1.0), EG (8.3)	–	(Miyazawa et al., 2007b)
Amberlyst-70[b] reused as recovered (Usage times:1)	4/16/0.15 + 0.01	Ir-ReO_x/SiO_2[c] 8 H_2/MPa	1,3-PDO (44.4), 1,2-PDO (8.0), 1-PrOH (39.4), 2-PrOH (8.0), Propane (0.2)	–	(Nakagawa et al., 2012)

(*continued on next page*)

Table 4 (*continued*)

Additives	Glycerol/ water/catalyst + additive (g)	Reaction conditions	Products (selectivity (%))	Products (yield (%))	References
		393 K 24 h 69.7%[d]			
Amberlyst-70[b] reused as recovered (Usage times: 2)	4/16/0.15 + 0.01	Ir-ReO_x/ SiO_2[c] 8 H_2/MPa 393 K 24 h 49.9%[d]	1,3-PDO (44.7), 1,2-PDO (9.4), 1-PrOH (36.1), 2-PrOH (8.5), Propane (1.4)	–	(Nakagawa et al., 2012)
Amberlyst-70[b] reused as recovered (Usage times:3)	4/16/0.15 + 0.01	Ir-ReO_x/ SiO_2[c] 8 H_2/MPa 393 K 24 h 37.5%[d]	1,3-PDO (48.6), 1,2-PDO (9.6), 1-PrOH (32.8), 2-PrOH (8.0), Propane (0.9)	–	(Nakagawa et al., 2012)
H-ZSM-5[b] reused as recovered (Usage times:1)	4/16/0.15 + 0.06	Ir-ReO_x/ SiO_2[c] 8 H_2/MPa 393 K 24 h 58.8%[d]	1,3-PDO (44.7), 1,2-PDO (9.3), 1-PrOH (35.3), 2-PrOH (9.4), Propane (1.3)	–	(Nakagawa et al., 2012)
H-ZSM-5[b] reused as recovered (Usage times:2)	4/16/0.15 + 0.06	Ir-ReO_x/ SiO_2[c] 8 H_2/MPa 393 K 24 h 36.1%[d]	1,3-PDO (50.3), 1,2-PDO (12.8), 1-PrOH (27.3), 2-PrOH (8.8), Propane (0.8)	–	(Nakagawa et al., 2012)
H-ZSM-5[b] reused as recovered (Usage times:3)	4/16/0.15 + 0.06	Ir-ReO_x/ SiO_2[c] 8 H_2/MPa 393 K 24 h 24.9%[d]	1,3-PDO (51.2), 1,2-PDO (13.9), 1-PrOH (26.1), 2-PrOH (8.8), Propane (<0.1)	–	(Nakagawa et al., 2012)

A: anode, C: cathode, CD: current density, E: applied potential, GCA: glycolic acid, GCD, glycidol, ACT: acetol, DHA: dihydroxyacetone, DEG, diethylene glycol, GLDA : glyceraldehyde, FA: formic acid, GA: glycolic acid, LA: lactic acid, EA: ethyl acetate, AA: acetic acid, 1,2-PDO: 1,2-propanediol, 1,3-PDO: 1,3-propanediol, HPA: hydroxypyruvic acid, 1-PrOH: 1-propanol, 2-PrOH: 2-propanol, EG: ethylene glycol and Others: 2-PrOH, 1-PrOH, acetol, 1,3-PDO, methanol and ethanol.

[a] Oxidizing agent.

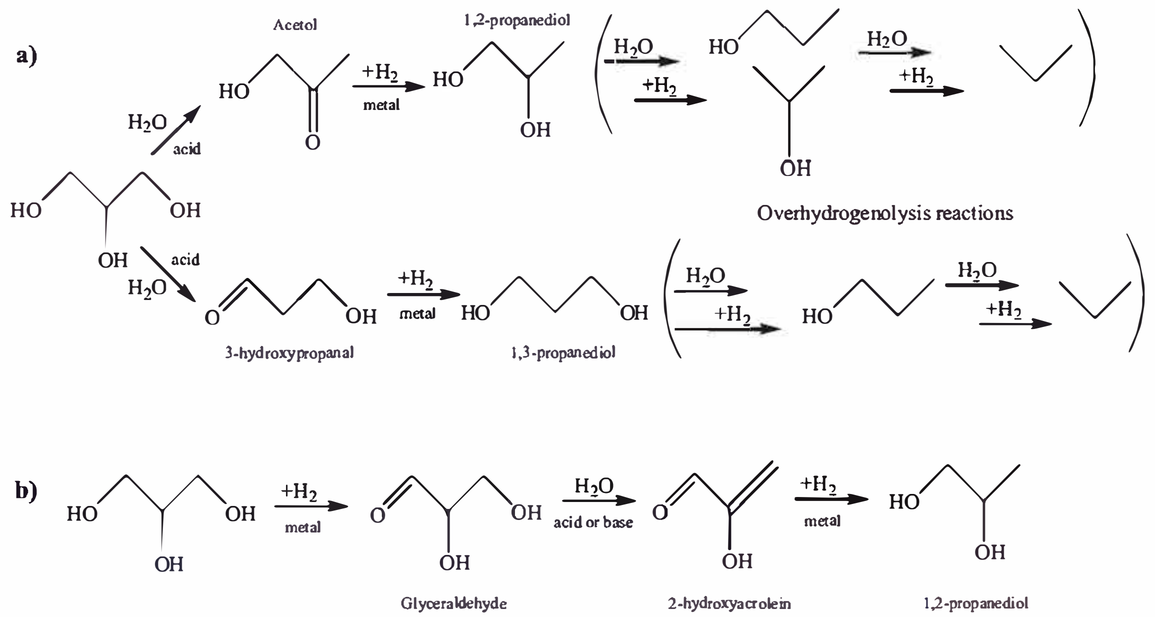
[b] Solid acid catalyst.

[c] Catalyst.

[d] Glycerol conversion.

as Amberlyst 15 and Amberlyst 70) and inorganic solid acids (like niobia (Nb_2O_5) and zicornia supported 12 tungstophosphoric $H_3PW_{12}O_{40}/ZrO_2$) to Ru/C catalyst have resulted high selectivity of 1,2 propanediol. These solid acids would be useful for further investigation in glycerol electrochemical conversion process. Amberlyst 15 was the most effective additive (co catalyst) used to enhance glycerol conversion and 1,2 propanediol selectivity in the glycerol hydrogenolysis. At 393 K (or 119 °C), 1,2 propanediol with 74.7% selectivity was obtained mainly by dehydration of glycerol to acetol catalysed by Amberlyst 15 and subsequent acetol hydrogenation to 1,2 propanediol on Ru/C (Miyazawa et al., 2007a). A heat resistant ion exchange resin Amberlyst 70 showed much higher reaction rate over Ru/C at 453 K (or 180 °C) compared to Amberlysts 15 at 393 K (Miyazawa et al., 2007b). Though, inorganic acids such as niobia (Nb_2O_5) and zicornia supported 12 tungstophosphoric $H_3PW_{12}O_{40}/ZrO_2$ are thermally more stable than these ion exchange resins and possess moderate acid sites which thereby, exhibited a better activity (Balaraju et al., 2009). Amberlyst would become deactivate as sulfonic acid group decomposed when the temperature at around 120 °C and above (Kusunoki et al., 2005; Miyazawa et al., 2006; Miyazawa et al., 2007a). A glycerol conversion of 62.8% with 1,2 propanediol (66.5% selectivity) was achieved using Nb_2O_5 solid acid at high temperature.

The formation of 1,2 propanediol and 1,3 propanediol were also related to the concentration of Lewis acid and Brønsted acid, respectively. Two types of mechanism routes have been proposed by many researchers as shown in Scheme 7. The dehydration glycerol with Lewis acid gives acetol, and hydrogenation of this intermediate yields 1,2 propanediol (Scheme 7**a**). In another mechanism route (Scheme 7**b**), glycerol is dehydrogenated to glyceraldehyde, this intermediate dehydrated to 2 hydroxyacrolein and thereby, generated 1,2 propanediol via hydrogenation (Nakagawa et al., 2014). Under Brønsted acid condition, glycerol will be dehydrated into 3 hydroxypropanal, however, acetol is thermodynamically stable than 3 hydroxypropanal which favouring acetol as main mechanism pathway. But, the cationic intermediate (secondary carbocation) for 3 hydroxypropanal is more stable compared to the acetol secondary carbocation, in other words, 3 hydroxypropanal is more kinetically favourable than acetol. Therefore, fast hydrogenation of 3 hydroxypropanal is important in 1,3 propanediol formation because further dehydration of 3 hydroxypropanal would yield acrolein (a precursor of propanols). In Nakagawa et al. (2012) work, 1,3 propanediol was obtained from glycerol hydrogenolysis over Ir ReOx/SiO_2 with the addition of various types of acids such as zeolites, silica alumina, ion exchange resin and sulfuric acid. Among these acids, solid acid catalyst (Amberlyst 70) was the most effective additive in enhancing the activity but in terms of additive reusability, H ZSM 5 is more suitable since it produced 1,3 propanediol with 51.2% selectivity after three times of usage. These additives could be applied in 1,3 propanediol formation during glycerol dehydration step into 3 hydroxypropanal intermediate.



Scheme 7. Mechanisms for 1,2-propanediol and 1,3-propanediol production from glycerol a) Two-step mechanism (Dehydration and hydrogenation) and b) Three-step mechanism (Dehydrogenation, dehydration and hydrogenation).

5. Future perspectives

From the above studies, the trend of research work is currently more emphasize to find out the alternative of the cost effective process and replace foreign metals with polymer based and carbon based electrodes. The good feature of those materials is they have the high surface area and huge pores size that could contribute to increasing the ion transport and electrolyte accessibility (Card et al., 1990; Tang et al., 2013), which lead to enhance the enrichment of target chemicals on the catalyst's surface and facilitate their diffusion onto the structure of catalysts (Shen et al., 2015). Lee et al. (2018) were the first researchers revealing the capability of mixed macroporous carbon black activated carbon (CBAC) (90 170 nm pore sizes) and mesoporous mixed carbon black diamond (CBD) (14 22 nm) electrodes to selectively produce 1,2 propanediol from glycerol, but, with the low yield. This work has been a good starter to develop cheaper carbon based electrocatalysts for this technology. More studies on inexpensive electrodes like heteroatom doped carbon based materials should be conducted in future to replace the expensive metal based electrodes (such as Pt catalyst). Several authors have reported the successful utilization of heteroatom doped carbon based materials for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and carbon dioxide electro reduction reaction (CO_2RR), resulting promising material design. As alternatives, doping carbon materials with heteroatoms elements (like nitrogen (N), fluorine (F), iodine (I), chlorine (C), bromine (Br), sulfur (S), silicon (Si), phosphorus (P), and their mixtures) could be used to increase the charge density and alter the inert carbon structures to be highly active, and make it suitable for glycerol electro oxidation and reduction technology (Yang et al., 2015; Hoyt et al., 2017). The discrepancy in electronegativity of these heteroatom dopants (P = 2.19, B = 2.04, S = 2.58, I = 2.66, Br = 2.96, N = 3.04, and Cl = 3.16 doped with carbon (C) (2.55) element would generate positive/negative charge density that can enable the electron transfer in the glycerol electrocatalytic oxidation and reduction processes (Gong et al., 2009; Song et al., 2016). Other than their bifunctionality characteristic, the increased of pores diameter in their structures could improve the catalytic activity with high active sites by decreasing oxygen adsorption and enhancing conductivity, thereby facilitating the reactions (Yadav et al., 2015; Song et al., 2016). The investigation of these carbon based materials in both alkaline and acidic media must be done to achieve the goal of practical industrial development of glycerol electrochemical conversion with low cost, sustainable and high performance electrocatalysts in future which rival those of Pt based and other expensive metals materials.

Despite the recognized developments in this field making a great progress, the implementation of this technology at large scale still faces few challenges such as the consumption of electricity in the current state may affect its green attribute. Most of the studies are still on a small scale and/or only work well for pure glycerol, and the real costs of production are uncertain. Therefore, more engineering research and the investigation of crude glycerol as starting material are essential to provide solutions to the challenges related to commercialization of this process. The separation and purification of products formed also must be taken into researchers' priority lists since the products generated are in a mixture form with the homogeneous electrolyte. A major disadvantage of using this homogeneous electrolyte for this process is the requirement of other technology to separate the electro oxidation and reduction products from its medium, leading to the additional cost in the operation. Thus, the future efforts should firstly focus on the mechanistic and kinetic studies to achieve the precise mechanism pathway with as highest as possible selectivity (purity) and yield of products. Besides, the electrolyte used in the current studies such as mineral acids (like HCl and H_2SO_4) are hazardous in handling, damaging the plant through their corrosiveness and add process difficulties using quenching and separation stages, which led to large volume of toxic and corrosive wastes. Thus, the replacement of these media with more eco friendly reagents like solid acids catalysts (such as zicornia, Amberlyst and silica) are highly needed. These solid acids catalysts could be separated easily and reused few times without lost its activity compared to the mineral acids that are currently used in the glycerol electrochemical conversion technology (Balaraju et al., 2009; Gupta and Paul, 2014). So that, the high purity of products could be obtained due to their selective reactions and improves this technology in future for the industrial scale.

6. Conclusion

This review has provided relevant information on electrochemical process of glycerol conversion which allows enhancing the rate of process and obtaining high selectivity and yield of desired products. The above discussion showed many researchers have recognized that the mediation of other molecules (like oxidizing agents, additives and adatoms) and the alteration of operating conditions (like applied potential, current density and temperature) could control both the activity and selectivity of desired products during the process. The synthesis of new hybrid materials as well as the variance of surface morphology and microstructure would enhance the active sites of materials and improve the catalytic activity. Additionally, primary hydroxyl oxidation to glyceraldehyde is more favoured on PtSn, PtIn and PtPb electrocatalysts, but when the catalyst is alloyed with other metals like Bi or Sb, the mechanism is shifted to DHA intermediate formation via secondary hydroxyl oxidation, which is only valid for Pt(1 1 1) electrode. The catalytic performance for Pt based electrodes are active under both acidic and alkaline conditions, nonetheless, Au based and Pd based electrodes are more stable in alkaline medium. Besides, the utilization of additives such as $Na_2S_2O_8$, H_2O_2 and TEMPO has changed the direction of mechanism path, principally via direct oxidation of primary or secondary hydroxyl group. Amberlyst 15 was the first heterogeneous mediator that have successfully used to selectively dehydrated glycerol to acetol and eventually, formed 1,2 propanediol. To further reduce the glycerol electrocatalytic oxidation and reduction technology cost, this review has anticipated to encourage more future work to push forward on development towards cost effective electrodes with better performance and less carbonaceous intermediates poisoning. The progress of polymer based and carbon based electrodes has started to develop as activated carbon based electrocatalysts have yielded high selectivity of electro reduction products. Furthermore, it can also be noted that this technology is an optional solution to simultaneously increase energy security and reduce dependence on fossil fuels worldwide.

Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgement

This work was supported by the Centre for Separation Science and Technology at University of Malaya and the Fundamental Research Grant Scheme (Project No: FP046 2017A) from the Ministry of Education (Department of Higher Learning).

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