

Selective Electroreduction of Glycerol to 1,2-Propanediol on a Mixed Carbon-Black Activated Carbon Electrode and a Mixed Carbon Black-Diamond Electrode

Ching Shya Lee,^{*,a,b} Mohamed Kheireddine Aroua,^{*,c,d} Wan Ashri Wan Daud,^a Patrick Cognet,^b Yolande Pérès,^b and Mohammed A. Ajeel^e

1,2-propanediol was selectively produced by electroreduction of glycerol in a two-compartment reactor. Two new kinds of cathode electrodes were evaluated: (i) mixed carbon black-activated carbon electrodes and (ii) mixed carbon black-diamond electrodes. These electrodes were compared with a conventional platinum electrode. With a reaction temperature of 80 °C, an electric current of 2.0 A, and ambient pressure, the mixed carbon black-activated carbon electrode demonstrated excellent performance and successfully reduced glycerol to 1,2-propanediol with a high selectivity of 86% and 74% glycerol conversion. The selectivity of 1,2-propanediol on the mixed carbon black-diamond electrode and the platinum electrode was 68% and 61%, respectively, with 88% glycerol conversion on the mixed carbon black-diamond electrode and 67% glycerol conversion on the platinum electrode. The authors propose a possible reaction mechanism for the formation of 1,2-PDO.

Keywords: Electroreduction; Glycerol; 1,2-Propanediol; Activated carbon; Diamond

Contact information: a: Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; b: Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, Toulouse, France; c: Research Centre for Nano-Materials and Energy Technology (RCNMET), School of Science and Technology, Sunway University, Bandar Sunway, 47500. Malaysia; d: Department of Engineering, Lancaster University, Lancaster, LA1 4YW, UK; e: Department of Chemistry, Al-Karkh University of Science, Baghdad 10066, Iraq; *Corresponding authors: leecs@um.edu.my; kheireddinea@sunway.edu.my

INTRODUCTION

1,2-Propanediol (1,2-PDO) has a high commercial value of \$117/kg (Sigma Aldrich). It is widely used to produce unsaturated polyester resins and antifreeze agent and is used in the cosmetics and food industries (Maris and Davis 2007). The global market of 1,2-PDO is driven by its major applications, particularly in the manufacture of unsaturated polyester resins. Its market price is expected to increase to \$4.2 billion/kt by 2019 (Future Market Insights 2016; Markets and Markets 2016). Generally, 1,2-PDO is commercially produced from propylene oxide with water *via* the hydroperoxide process or the chlorohydrin process (Yadav *et al.* 2012). Recently, bioglycerol, the byproduct obtained through the transesterification process of biodiesel production, has attracted substantial attention as a renewable feedstock for the synthesis of 1,2-PDO *via* the catalytic hydrogenolysis pathway.

Previous studies demonstrated the effectiveness of various catalyst systems in glycerol hydrogenolysis. These systems combine noble metals including Ru, Pd, Rh, and Pt with other transition metals such as Zn, Cr, and Cu with silica, zeolite, aluminium

oxide, or activated carbon supports (Rode *et al.* 2010). Kusunoki *et al.* (2005) reported that an Ru/C catalyst converted 79% glycerol to 1,2-PDO with a selectivity of 82% under the reaction conditions of 120 °C and 4 MPa H₂ pressure for 10 h in the presence of Amberlyst-15. However, Ru alone could effectively enhance the byproduct reaction by cracking glycerol into smaller compounds such as ethylene glycol, ethanol, methanol, and methane (Kusunoki *et al.* 2005). Maris *et al.* (2007) indicated that hydrogenolysis on Pt or bimetallic Pt/Ru supported by C resulted in high selectivity for lactate rather than 1,2-PDO at high pH or in the presence of base (Maris and Davis 2007). In the catalytic process, reactions are usually conducted under high temperature and high pressure conditions. As such, the cost of production is high due to high energy usage. The reaction conditions, types of catalysts, glycerol conversion percentages, and selectivity for 1,2-PDO are summarized in Table 1.

Table 1. Summary of Glycerol Conversion, 1,2-PDO Yield, and Selectivity Obtained from the Catalytic Hydrogenolysis or Microbial Conversion of Glycerol

Catalyst/ Bacterial Strain	T (°C)	P _{H₂} (bars)	Time (h)	Glycerol Conversion (%)	1,2-PDO		Reference
					Y (%)	S (%)	
Rh _{0.02} Cu _{0.4} /Mg _{5.6} Al _{1.98} O _{8.57}	180	2.0	10	91	-	98.7	(Xia <i>et al.</i> 2012)
Ru/SiO ₂	240	8.0	5	21.7	-	60.5	(Vasiliadou and Lemonidou 2011)
CuO	200	Ambient	180 g _{cat} min/mol	100	-	60	(Dieuzeide <i>et al.</i> 2016)
Cu _{0.4} /Mg _{6.28} Al _{1.32} O _{8.26}	210	3.0 (N ₂)	10	95.1	-	92.2	(Xia <i>et al.</i> 2013)
Cu/MgO	220	0.75	14	100	-	95.5	(Pandhare <i>et al.</i> 2016)
Cu-Al Mixed Oxides	220	7.0	24	74.3	58.6	78.9	(Valencia <i>et al.</i> 2015)
Cu/MgO	210	4.5	12	96.6	-	92.6	(Pandhare <i>et al.</i> 2016)
Ru-Cu	180	8.0	24	100	-	78.5	(Liu <i>et al.</i> 2012)
CuO/MgO	180	3.0	20	72.0	-	97.6	(Yuan <i>et al.</i> 2010)
Pt Impregnated NaY zeolite	230	4.2	15	85.4	-	64.0	(D'Hondt <i>et al.</i> 2008)
Cu-Cr(Ba)	220	5.2	Batch: 5	34	-	84	(Rode <i>et al.</i> 2010)
			Continuous: 800	65		>90	
Cu/Al ₂ O ₃	205	2.0	23	88.7	-	94.3	(Wolosiak-Hnat <i>et al.</i> 2013)

T, reaction temperature; P_{H₂}, hydrogen pressure; Y, yield; S, selectivity

Electrolysis is an alternative pathway to overcome the shortcomings of current methods. This method is simple, robust, and can operate under ambient pressure and low reaction temperature. In previous studies, the electrochemical conversion of glycerol has been based on electro-oxidation. However, the study of the electroreduction of glycerol into 1,2-PDO has not been reported previously. Glycerol can be electro-oxidised into

various hydroxyl acids such as glycolic acid, mesoxalic acid, and glyceric acid (Simões *et al.* 2010, 2011; Zhang *et al.* 2014). The selectivity of these products is dependent on the pH of the reaction medium and the type of electrode materials (Avramov-Ivić *et al.* 1991, 1993; Roquet *et al.* 1994; Yildiz and Kadirgan 1994).

Activated carbon, which is commonly functionalized with polymer or incorporated with noble metals such as Pt, Pd, Rh, and Au, is broadly used as an electrode in electrochemical studies (Card *et al.* 1990; Bambagioni *et al.* 2009; Kwon *et al.* 2012). Activated carbon with a high specific surface area ($1000 \text{ m}^2/\text{g}$) can be produced from readily available biomass precursors such as coal, coke, saw dust, peat, wood char, seed hulls, and palm kernel shell (Omar *et al.* 2003; Kalderis *et al.* 2008; Foo and Hameed 2011; Elmouwahidi *et al.* 2012; Foo and Hameed 2013; He *et al.* 2013; Lee *et al.* 2013). The large surface area and pore size of the carbon support can improve ion transport and electrolyte accessibility (Tang *et al.* 2013).

Another material which is currently widely used in the electrochemical study is doped diamond electrode. In the study by Kraft (2007), doped diamond electrode was compared with platinum electrode in the region between oxygen and hydrogen evolution in $0.2 \text{ M H}_2\text{SO}_4$ by using cyclic voltammetry. The result obtained shows that doped diamond electrode has a wider potential window and high oxygen as well as hydrogen evolution overpotential (Kraft 2007). This striking feature distinguishes the doped diamond electrode from common electrode materials, such as Pt, Au, or mixed metal electrodes. The doped diamond electrode demonstrates high electrochemical stability under severe conditions (Panizza and Cerisola 2005; Alfaro *et al.* 2006). However, the surface area of doped diamond electrode is restricted by the size of chemical vapor deposition chamber.

A carbon black diamond (CBD) composite electrode, which has no limitation on the shape and dimension, was investigated for the first time in our laboratory for electrochemical oxidation of organic pollutants, such as phenol and benzoquinone. The CBD electrode offered a wide potential window and inert surface. Its potential window decreased with increasing of carbon black (CB) percentage in the electrode. The 5% CB presented a similar potential window as the conventional boron doped diamond electrode (Ajeel *et al.* 2015c). However, results reported that 20% CBD electrode achieved a high removal efficiency (96.5%) for benzoquinone (200 g/L) after 20 min of oxidation (Ajeel *et al.* 2015b). In addition, CBD electrode showed a high selectivity in phenol oxidation in comparison with the conventional Pt electrode, whereby fumaric acid was the only chemical compound observed after the electro-oxidation process (Ajeel *et al.* 2015c). Later, an activated carbon composite (ACC) electrode was prepared and used as anode electrode for 2-chlorophenol electro-oxidation. The performance of ACC was compared with CBD (20% CB). After 6 h of electro-oxidation, the degradation efficiencies of ACC and CBD on 2-chlorophenol were 82.5% and 96.0%, respectively. ACC offered higher surface area by fourfold compared to that of CBD, and it exhibited the same degradation rate as the CBD electrode (Ajeel *et al.* 2015a). Moreover, the price of activated carbon and diamond materials are lower than that of noble metal catalysts (Pt, Pd, Rh, and Au). The cost of each material per gram is displayed in Table 2 (Sigma Aldrich). Due to their high selectivity and cost effectiveness advantages, two environmentally friendly, low-cost carbon-based electrodes (mixed carbon black-activated carbon electrodes (CBAC) and mixed carbon black-diamond (CBD) electrodes) are proposed in the present study.

Table 2. Common Materials Used for Catalyst Preparation

Type of Material	CAS Number	% Purity	Price (USD \$/g)
Platinum*	7440-06-4	99	2015.00
Palladium*	7440-05-3	99	1260.00
Rhodium*	7440-16-6	99	506.00
Gold*	7440-57-5	99	347.00
Diamond*	7782-40-3	97	97.20
Activated Carbon**	7440-44-0	99	0.11
*in nanopowder form			
**in powder form			

In this work, 20% CBAC and 20% CBD were prepared and used as the cathode electrode for electrochemical conversion of glycerol. The electrochemical conversion was carried out in a two-compartment electrochemical cell to avoid the mixed oxidation-reduction process that occurs in a single-compartment electrochemical cell (Saila *et al.* 2015). Hence, enhanced selectivity to 1,2-PDO was expected. The glycerol conversion and product selectivity were compared with those obtained using the conventional Pt electrode. A potential reaction mechanism is proposed.

EXPERIMENTAL

Electrode Preparation

A CBAC electrode (with a geometrical surface area of 14 cm²) was prepared by mixing 80 wt.% activated carbon powder (AC) (99.5% purity with an average particle size of 100 μm and a 950 m²/g specific surface area) (Sigma Aldrich, Germany) and 20 wt.% carbon black nanopowder (CB) (99% purity with an average particle size of 13 nm and a 550 m²/g specific surface area) (Alfa-chemicals, United Kingdom) to a total weight of 3.0 g. The CBD electrode (with a geometrical surface area of 14 cm²) was prepared by blending 20 wt.% CB nanopowder and 80 wt.% nanodiamond powder (98.3% purity with an average particle size of 3 nm to 10 nm and a 200 m²/g to 400 m²/g specific surface area) (Sigma Aldrich). CB nanopowder was added during the electrode preparation to increase the conductivity of the electrode (Ajeel *et al.* 2015c). The ratio of each composition used in the electrode preparation was described in an earlier study on the electro-degradation of 2-chlorophenol. Ajeel (*et al.* 2015a) reported that the AC and diamond electrodes with 20 wt.% CB nanopowder had a removal efficiency of 2-chlorophenol as high as 83% and 96%, respectively. Therefore, a similar electrode was prepared and used as a cathode electrode in this study.

The pre-mixed powder was added into a mixture containing 20% v/v of polytetrafluoroethylene and 80% v/v of 1,3-propanediol to obtain a powder-to-liquid ratio of 1:2. The slurry was pressed neatly and oven dried in accordance with the following heating temperature program: 100 °C for 2 h, 180 °C for 1 h, 250 °C for 1 h, and 350 °C for 30 min to allow complete sintering of the powder and increase electrode hardness (Ajeel *et al.* 2015a).

Scanning Electron Microscopy (SEM)

The morphology of the CBAC and CBD electrodes were studied by scanning electron microscopy using a Hitachi SU-8000 instrument (Tokyo, Japan) equipped with

an energy dispersive X-ray (EDX) analyser. The element content in the electrode was determined by EDX.

Measurement of Active Surface Area

The active surface areas of CBAC and CBD electrodes (with geometrical surface areas of 0.45 cm²) were measured by chronoamperometry analysis in 0.005 M ferrocyanide solution (K₄Fe(CN)₆) (≥ 99.95% purity) (Sigma Aldrich) containing 0.1 M KH₂PO₄ (purity ≥ 99%) (Sigma Aldrich). The test was performed with an Autolab Potentiostat from Metrohm (Model PGSTAT101, Switzerland). The active surface areas of the CBAC and CBD electrodes were obtained using the Cottrell equation (Ajeel *et al.* 2015a),

$$I = \frac{nFAD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (1)$$

where I is the current (A), n is the number of electrons, A is the active surface area of the electrode (cm²), D is the diffusion coefficient (6.20 × 10⁻⁶ cm²/s), C_0 is the bulk concentration of K₄Fe(CN)₆ (mol/cm³), F is the Faraday constant 96487 (C/mol), and t is the time (s).

Electrochemical Reduction Behavior

The electroreduction of glycerol was carried out in a two-compartment reactor separated by a cation exchange membrane (Nafion-117, Fuel Cell Store, United States), as shown in Fig. 1. Each compartment was filled with 0.25 L of 0.30 M glycerol solution. Next, 24.0 g of Amberlyst-15 and 10.0 g of Na₂SO₄ were dispersed into the entire glycerol solutions. Amberlyst-15 was used as an acid catalyst in this study. The strong sulfonic acid group in Amberlyst-15 allows it to serve as an excellent catalyst during the electrolysis performance. The application of Amberlyst-15 in the electrochemical conversion of glycerol was previously studied by the author and was found that the presence of Amberlyst-15 can enhanced the glycerol conversion, product selectivity and yield.

Pt (geometrical surface area of 22 cm²) was used as the anode electrode. Three types of cathode materials were studied: Pt (geometrical surface area of 33.0 cm²), CBAC (geometrical surface area of 14.1 cm²), and CBD (geometrical surface area of 14.1 cm²). A constant current (2.0 A) was supplied to the system, and the reaction temperature was controlled at 80 °C for 8 h.

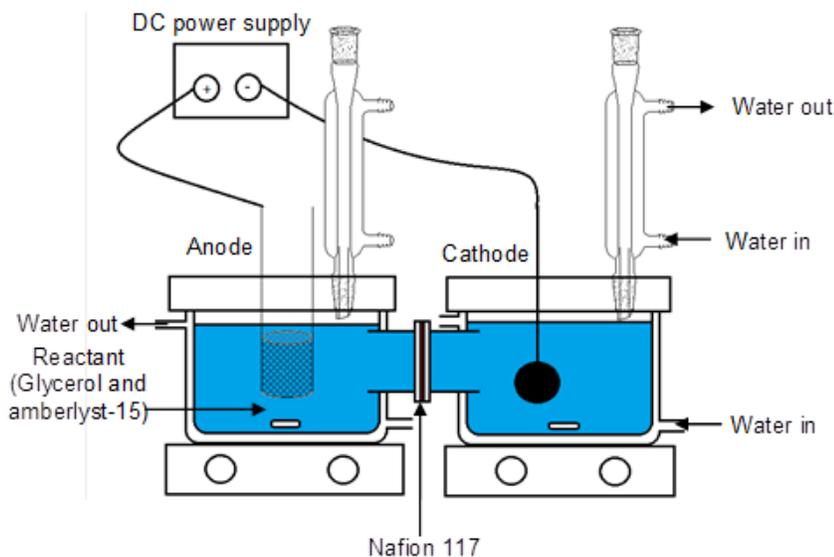


Fig. 1. Electrochemical set-up

Product Characterization and Quantification

The products were separated and characterized by gas chromatography-mass spectroscopy (GC-MS) (Agilent Model 7890, United State) with an attached ZB-Wax column (30 m × 0.25 mm × 0.25 μm). High purity helium (> 99.99%) was used as the carrier gas at a constant flow of 2.0 mL min⁻¹. The initial oven temperature was set to 45 °C, maintained for 5 min, and then increased at a rate of 10 °C min⁻¹ to reach the final temperature of 240 °C, which was maintained for 5 min. The injection volume was 1 μL. The results were compared with the chemical standards and MS library (ChemStation software) (Agilent). The glycerol conversion and selectivity were calculated by Eqs. 2 and 3, respectively.

$$\text{Glycerol conversion (\%)} = \frac{\text{Amount of glycerol converted (in mole C)}}{\text{Total amount of glycerol in reactant (in mole C)}} \times 100 \% \quad (2)$$

$$\text{Product selectivity (\%)} = \frac{\text{Amount of product (in mole C)}}{\text{Sum of all products (in mole C) in liquid phase}} \times 100 \% \quad (3)$$

RESULTS AND DISCUSSION

CBAC and CBD Electrode Characterization

Scanning electron microscopy was used to investigate the morphologies of the CBAC and CBD electrodes. Scans were performed at high magnification (50000×) with image resolutions of 1.00 μm. The SEM image for the CBAC electrode in Fig. 2a shows that CBAC exhibited high porosity with average pore sizes ranging from 90 nm to 170 nm. The detectable pore sizes for the CBD electrode were smaller (around 14 nm to 22

nm) (Fig. 2b) and lower than those of the CBAC electrode. The mesoporous and macroporous structure in both electrodes can help to hold or trap the reaction intermediate, thus enhancing the product selectivity (Qi *et al.* 2014; Zhang *et al.* 2014).

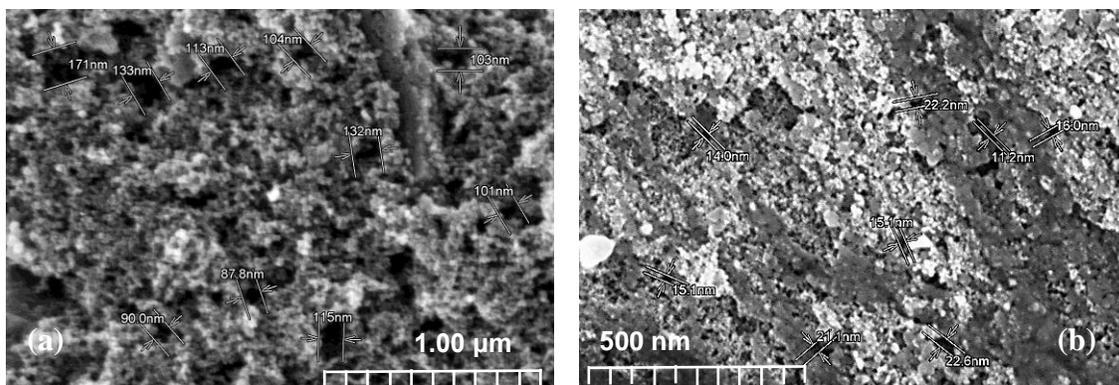


Fig. 2. SEM images of (a) CBAC and (b) CBD electrodes

The elements present in the electrodes were determined using SEM-EDX, and the spectra for the CBAC and CBD electrodes are shown in Fig. 3a and Fig. 3b, respectively. The CBAC electrode contained three elements, namely carbon (C), fluorine (F), and oxygen (O). Carbon was the major element in the CBAC electrode, with a nominal value of 75 wt.%. Fluorine and O could be the elements from the binder and solvent (polytetrafluoroethylene and 1,3-propanediol) used in the electrode preparation with corresponding values of 21 wt.% and 4% wt.%, respectively. The CBD electrode contained the same elements, namely C (92 wt.%), F (6 wt.%), and O (1 wt.%).

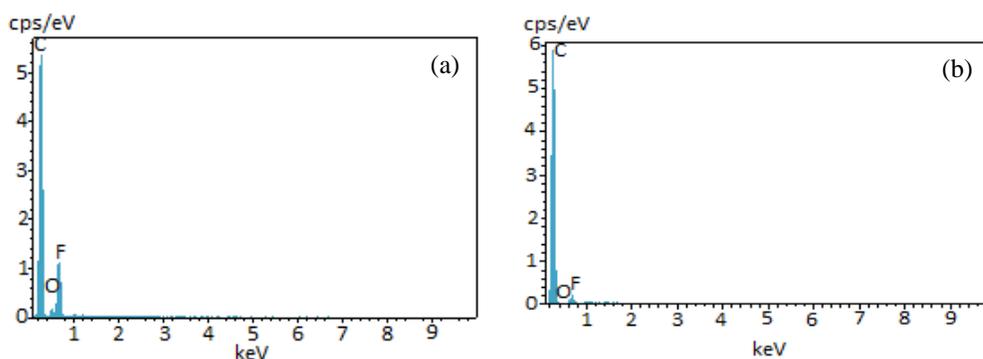


Fig. 3. SEM-EDX spectrum for (a) CBAC and (b) CBD electrodes

Cathodic Reduction Behavior of Glycerol on the CBAC and CBD Electrodes

Prior to the electrochemical study, the electroreduction behavior of glycerol was examined on the CBAC and CBD electrodes by CV analysis in the presence of Amberlyst-15. Blank CVs without glycerol were prepared on the CBAC and CBD electrodes. Scanning was performed from + 0.05 V to -1.80 V at a scan rate of 0.2 V s⁻¹. Figure 4 shows the cyclic voltammogram of the CBAC and CBD electrodes. Compared with the CVs in the absence of glycerol, no obvious cathodic peaks were observed on either electrode in the presence of glycerol. These results might have been due to the lack of direct electron transfer with glycerol on the CBAC and CBD electrodes during the electroreduction process. The electroreduction of glycerol might have occurred indirectly

(Ajeel *et al.* 2015a). Despite the absence of reduction peaks for glycerol on the CBAC and CBD electrodes, the cathodic current slightly increased for the glycerol solution, showing that electroreduction on the CBAC and CBD electrodes was favourable in the presence of glycerol.

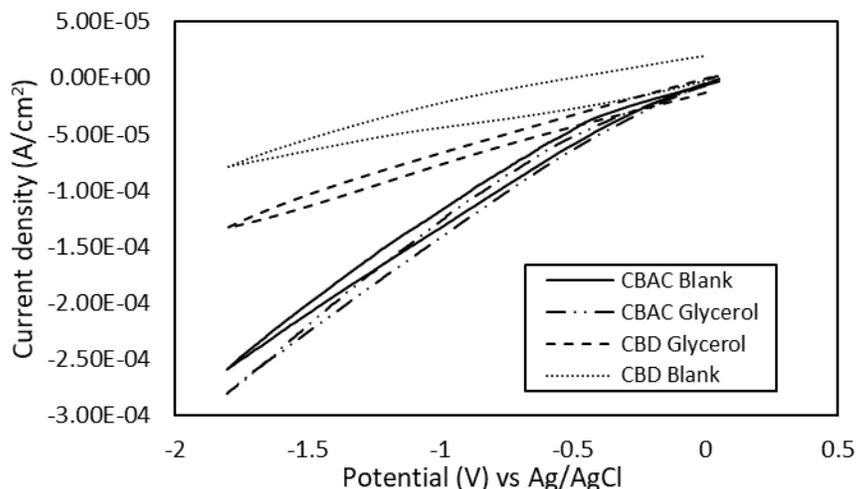


Fig. 4. CV of CBAC and CBD electrodes in blank solution and aqueous solution of glycerol in the presences of Amberlyst-15 with a scan range from + 0.05 to - 1.80 V and a scan rate of 0.2 V/s

Electroreduction of Glycerol to 1,2-PDO

The electroreduction of glycerol was performed in the presence of Amberlyst-15, at a temperature of 80 °C, and an electric current of 2.0 A over the CBAC and CBD electrodes. The results were then compared with those of the Pt electrode, as shown in Fig. 5. Glycerol was converted to 67%, 74%, and 88% on the Pt, CBAC, and CBD cathodes, respectively. The first-order kinetic models for the reaction over the Pt, CBAC, and CBD electrodes are shown in Fig. 6. In agreement with Kongjao *et al.* (2011), the electrolysis on the Pt electrode only fit the first-order kinetic model well at 2 h. The rate constants on the Pt, CBAC, and CBD electrodes were 0.191 h⁻¹, 0.165 h⁻¹, and 0.197 h⁻¹, respectively.

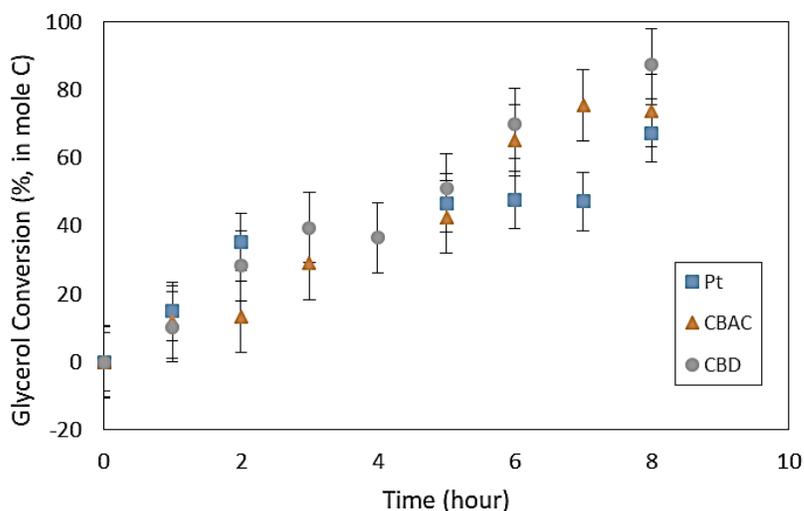


Fig. 5. Glycerol conversion profile through the electroreduction of glycerol in the presence of Amberlyst-15 at 2.0 A and 80 °C over Pt, CBAC, and CBD cathode electrodes

According to the GC-MS chromatogram in Fig. 7, 1,2-PDO, acetol, and diethylene glycol (DEG) were found in all samples. In the presence of H^+ ions supplied by Amberlyst-15, glycerol was first dehydrated into acetol (Ishiyama *et al.* 2013). In the catalytic hydrogenolysis pathway, acetol was further reduced to 1,2-PDO (Chaminand *et al.* 2004; Huang *et al.* 2009). This phenomenon could explain the absence of reduction peaks in the CV analysis as the glycerol underwent indirect electroreduction. During electrolysis, the reduction compound 1,2-PDO was produced through the electroreduction of the intermediate (acetol) instead of the direct reduction of glycerol. Ethylene glycol was produced *via* C-C bond cleavage during the reduction process (Nakagawa and Tomishige 2011). Diethylene glycol is formed by the coupling of ethylene glycols.

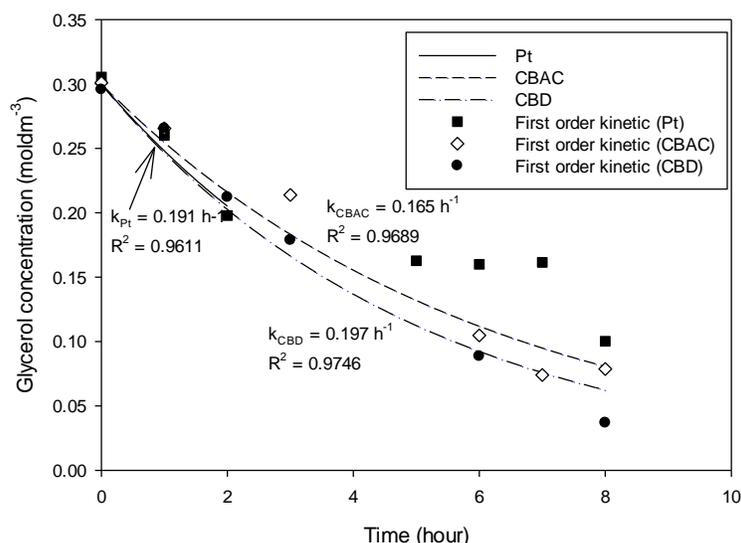


Fig. 6. First-order kinetic model of the electroreduction of glycerol in the presence of Amberlyst-15 at 2.0 A constant current and 80 °C over the Pt, CBAC, and CBD cathode electrodes

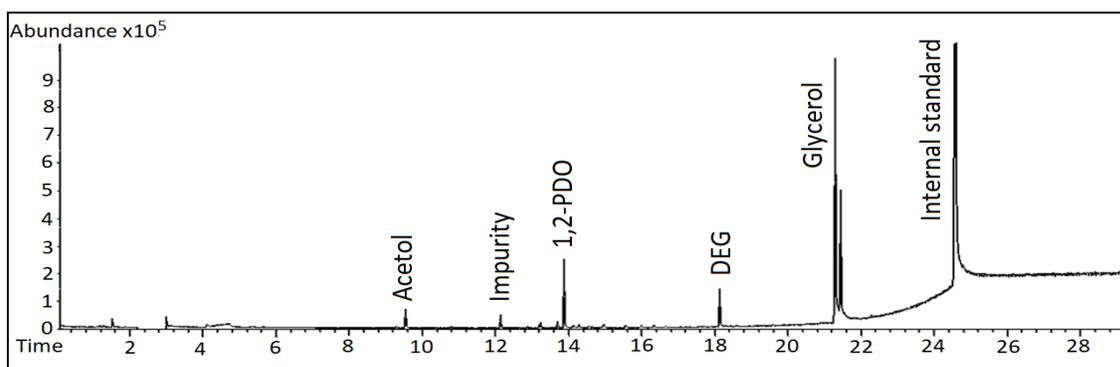


Fig. 7. The GC-MS chromatogram of the products obtained from the electroreduction of glycerol in the presence of Amberlyst-15 on the Pt, CBAC, or CBD cathode electrodes at 80 °C and 2.0 A, after 8 h or reaction.

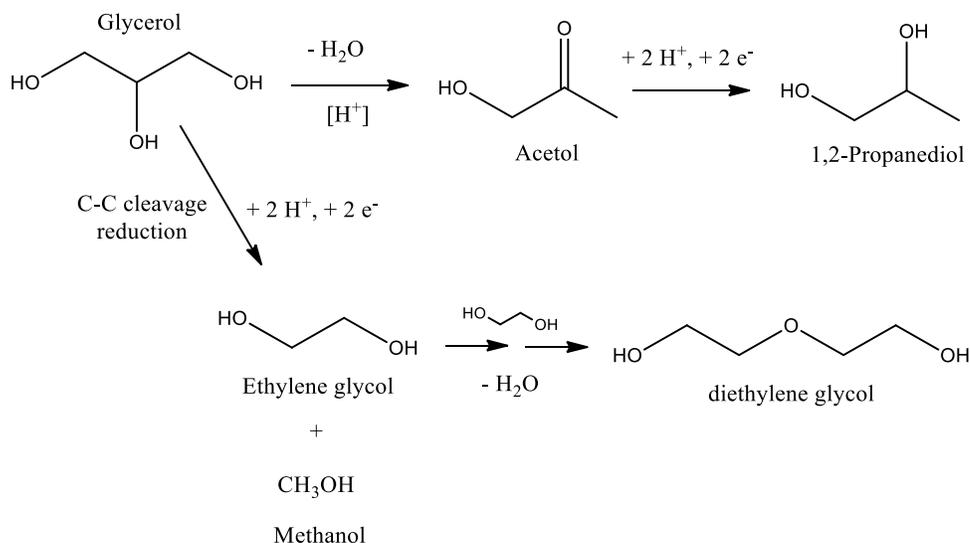


Fig. 8. Proposed reaction mechanism for the electroreduction of glycerol

Although DEG was obtained as a side product in this study, it is also a valuable glycerol derivative. Compared with the price of crude glycol, the market value for DEG is significantly higher at \$ 134/kg (Sigma Aldrich). The reaction mechanism is proposed in Fig. 8.

In the initial stage of the reaction, 1,2-PDO was not detected in any specimen. After 1 h, 2 h, and 3 h of electrolysis, 1,2-PDO was observed in small amounts on the CBAC, Pt, and CBD electrodes, respectively. The highest product selectivity for 1,2-PDO (86%) was obtained on the CBAC electrode with 74% glycerol conversion after 8 h. Acetol and DEG were also obtained in the reaction mixture with a total selectivity of 14%. Based on the product selectivity graph in Fig. 9, the reduction performances on the Pt and CBD electrodes were slightly lower compared with the CBAC electrode. The 1,2-PDO selectivity of 61% (on Pt) and 68% (on CBD) were obtained after 8 h of reaction time. SEM analysis demonstrated that the surface of the CBAC electrode had high porosity with larger pore sizes than the CBD electrode. This result indicated that the CBAC electrode had higher active surface areas and larger pore sizes than those of the CBD and Pt electrodes. The diffusion limit of the substrates can be reduced when the pores size increase, thus improving ion transport during electrolysis and increasing the product selectivity as well as glycerol conversion (McMorn *et al.* 1999).

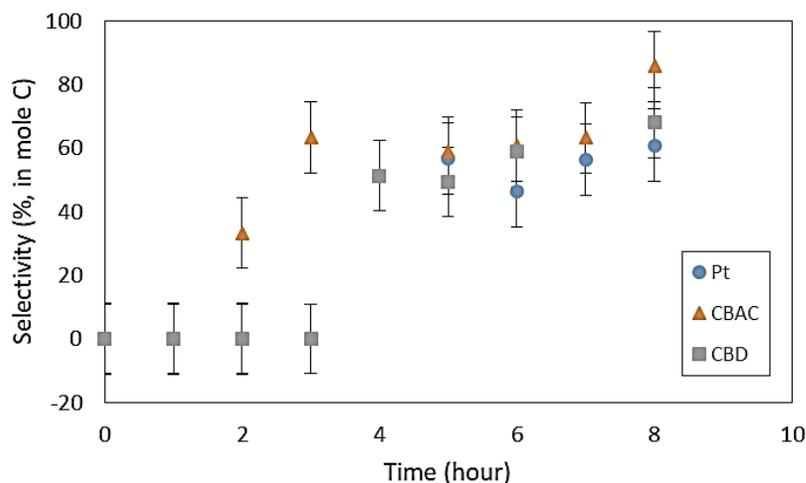


Fig. 9. Selectivity for 1,2-PDO from the electroreduction of glycerol in the presence of Amberlyst-15 over Pt, CBAC, and CBD electrodes at 80 °C and 2.0 A electric current

The chronoamperometry analysis revealed that the CBAC and CBD electrodes with the same geometrical surface area of 14 cm² had active surface areas of 227 cm² and 88 cm², respectively. The Pt electrode (geometrical surface area of 33 cm²) had an active surface area of only 43 cm². The high active surface area of the CBAC electrode improved the electrocatalytic activity by increasing electrolyte accessibility and improving ion transportation (Tang *et al.* 2013). Table 3 summarizes the product selectivity and glycerol conversion on the Pt, CBAC, and CBD electrodes.

Table 3. Electroreduction of Glycerol over Pt, CBAC, and CBD Electrodes; Selectivity for 1,2-PDO, Acetol, and Diethylene Glycol after 8 h Electrolysis Time

Electrode		Amberlyst-15 (g)	<i>I</i> (A)	<i>V</i> (V)	<i>T</i> (°C)	Glycerol Conversion		Selectivity (% in mole C)		
A	C					%	<i>k</i> (h ⁻¹)	12-PDO	Acetol	DEG
Pt	Pt	24.0	2.0	23	80	67	0.191 (2 h)	61	24	15
Pt	CBAC	24.0	2.0	24	80	74	0.165	86	3	11
Pt	CBD	24.0	2.0	23	80	88	0.197	68	17	15

Note: A, Anode; C, cathode; *I*, current; *T*, temperature; *V*, potential

Research Outlook

Based on results obtained in prior studies (Table 1), this study led to a comparable or better selectivity for 1,2-PDO under milder reaction conditions. Electrolysis was performed at ambient pressure and a reaction temperature of 80 °C. Moreover, peak selectivity for 1,2-PDO was achieved after 8 h of electrolysis time. Shortening the reaction time can reduce the contact time of glycerol with the electrocatalyst, thereby stopping the production of unfavorable byproducts. When glycerol reacts under high reaction temperature and pressure for many hours, the glycerol C-C bond breaks, which leads to further formation of small unwanted compounds such as ethylene glycol (Rode *et al.* 2010). This study also showed that fewer compounds were formed during electrolysis than during the fermentation process.

In addition, the price of the electrode materials must be inexpensive to compete effectively with the current available catalyst and electrocatalyst. Based on the costs

shown in Table 2, the CBAC and CBD electrodes are relatively cheap compared with noble metal catalysts (Pt, Pd, Rh, and Ru). Furthermore, AC can be easily obtained from biomass feedstocks such as saw dust, seed hulls, and palm kernel shell. In Malaysia, palm kernel shell is the main source for AC because it is one of the most prominent agricultural wastes obtained from the oil palm industry (Abdullah *et al.* 2011).

CONCLUSIONS

1. In this study, the direct electroreduction of glycerol was examined. Glycerol was successfully reduced to 1,2-PDO on the two new cathode materials of CBAC and CBD.
2. The highest 1,2-PDO selectivity of 86% was obtained after 8 h of reaction time with a maximum glycerol conversion of 74% occurring on the CBAC electrode.
3. On the CBD electrode, the glycerol conversion percentage was 88% with a 1,2-PDO selectivity of 68%.
4. Acetol and DEG were also obtained, but in very low product selectivity.
5. These findings successfully provided a new approach for glycerol electroreduction studies.

ACKNOWLEDGMENTS

The authors are thankful for the support of the Centre for Separation Science and Technology at University of Malaya, the Laboratoire de Génie Chimique at Campus INP-ENSIACET, and the Federation INCREASE. The authors also acknowledge financial support of the High Impact Research Grant (HIR Grant No: HIR/MOHE/ENG/59) and the Postgraduate Research Grant (PPP Grant No: PG006-2012B) from the University of Malaya and the partial financial support for the Dual PhD candidate from the French Embassy in Malaysia.

REFERENCES CITED

- Abdullah, M. O., Tan, I. A. W., and Lim, L. S. (2011). "Automobile adsorption air-conditioning system using oil palm biomass-based activated carbon: A review," *Renewable and Sustainable Energy Reviews* 15(4), 2061-2072. DOI: 10.1016/j.rser.2011.01.012
- Ajeel, M. A., Aroua, M. K., and Daud, W. M. A. W. (2015a). "Anodic degradation of 2-chlorophenol by carbon black diamond and activated carbon composite electrodes," *Electrochimica Acta* 180, 22-28. DOI: 10.1016/j.electacta.2015.08.062
- Ajeel, M. A., Aroua, M. K., and Daud, W. M. A. W. (2015b). "p-Benzoquinone anodic degradation by carbon black diamond composite electrodes," *Electrochimica Acta* 169, 46-51. DOI: 10.1016/j.electacta.2015.04.037
- Ajeel, M. A., Aroua, M. K., and Daud, W. M. A. W. (2015c). "Preparation and characterization of carbon black diamond composite electrodes for anodic

- degradation of phenol," *Electrochimica Acta* 153, 379-384. DOI: 10.1016/j.electacta.2014.11.163
- Alfaro, M. A. Q., Ferro, S., Martínez-Huitle, C. A., and Vong, Y. M. (2006). "Boron doped diamond electrode for the wastewater treatment," *Journal of the Brazilian Chemical Society* 17, 227-236. DOI: 10.1590/S0103-50532006000200003
- Avramov-Ivić, M., Léger, J. M., Beden, B., Hahn, F., and Lamy, C. (1993). "Adsorption of glycerol on platinum in alkaline medium: Effect of the electrode structure," *Journal of Electroanalytical Chemistry* 351(1-2), 285-297. DOI: 10.1016/0022-0728(93)80240-1
- Avramov-Ivić, M. L., Leger, J. M., Lamy, C., Jović, V. D., and Petrović, S. D. (1991). "The electro-oxidation of glycerol on the gold(100)-oriented single-crystal surface and poly crystalline surface in 0.1 M NaOH," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 308(1-2), 309-317. DOI: 10.1016/0022-0728(91)85075-Z
- Bambagioni, V., Bianchini, C., Marchionni, A., Filippi, J., Vizza, F., Teddy, J., Serp, P., and Zhiani, M. (2009). "Pd and Pt–Ru anode electrocatalysts supported on multi-walled carbon nanotubes and their use in passive and active direct alcohol fuel cells with an anion-exchange membrane (alcohol = methanol, ethanol, glycerol)," *Journal of Power Sources* 190(2), 241-251. DOI: 10.1016/j.jpowsour.2009.01.044
- Card, J. C., Valentin, G., and Storck, A. (1990). "The activated carbon electrode: A new, experimentally verified mathematical model for the potential distribution," *Journal of The Electrochemical Society* 137(9), 2736-2745. DOI: 10.1149/1.2087050
- Chaminand, J., Djakovitch, L. A., Gallezot, P., Marion, P., Pinel, C., and Rosier, C. (2004). "Glycerol hydrogenolysis on heterogeneous catalysts," *Green Chemistry* 6(8), 359-361. DOI: 10.1039/B407378A
- D'Hondt, E., Van de Vyver, S., Sels, B. F., and Jacobs, P. A. (2008). "Catalytic glycerol conversion into 1,2-propanediol in absence of added hydrogen," *Chemical Communications* (45), 6011-6012. DOI: 10.1039/B812886C
- Dieuzeide, M. L., Jobbagy, M., and Amadeo, N. (2016). "Vapor-phase hydrogenolysis of glycerol to 1,2-propanediol over Cu/Al₂O₃ catalyst at ambient hydrogen pressure," *Industrial & Engineering Chemistry Research* 55(9), 2527-2533. DOI: 10.1021/acs.iecr.5b03004
- Elmouwahidi, A., Zapata-Benabithé, Z., Carrasco-Marín, F., and Moreno-Castilla, C. (2012). "Activated carbons from KOH-activation of argan (*Argania spinosa*) seed shells as supercapacitor electrodes," *Bioresource Technology* 111, 185-190. DOI: 10.1016/j.biortech.2012.02.010
- Foo, K. Y. and Hameed, B. H. (2011). "Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K₂CO₃ activation," *Bioresource Technology* 102(20), 9814-9817. DOI: 10.1016/j.biortech.2011.07.102
- Foo, K. Y. and Hameed, B. H. (2013). "Utilization of oil palm biodiesel solid residue as renewable sources for preparation of granular activated carbon by microwave induced KOH activation," *Bioresource Technology* 130, 696-702. DOI: 10.1016/j.biortech.2012.11.146
- Future Market Insights. (2016). *Biobased Propylene Glycol Market: Global Industry Analysis and Opportunity Assessment 2014 – 2020*, (<http://www.futuremarketinsights.com/reports/global-biobased-propylene-glycol-market>). Accessed 20-6-2016
- He, X., Ling, P., Qiu, J., Yu, M., Zhang, X., Yu, C., and Zheng, M. (2013). "Efficient

- preparation of biomass-based mesoporous carbons for supercapacitors with both high energy density and high power density," *Journal of Power Sources* 240, 109-113. DOI: 10.1016/j.jpowsour.2013.03.174
- Huang, L., Zhu, Y., Zheng, H., Ding, G., and Li, Y. (2009). "Direct conversion of glycerol into 1,3-propanediol over Cu-H₄SiW₁₂O₄₀/SiO₂ in vapor phase," *Catalysis Letters* 131(1-2), 312-320. DOI: 10.1007/s10562-009-9914-1
- Ishiyama, K., Kosaka, F., Shimada, I., Oshima, Y., and Otomo, J. (2013). "Glycerol electro-oxidation on a carbon-supported platinum catalyst at intermediate temperatures," *Journal of Power Sources* 225, 141-149. DOI: 10.1016/j.jpowsour.2012.10.035
- Kalderis, D., Bethanis, S., Paraskeva, P., and Diamadopoulos, E. (2008). "Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times," *Bioresource Technology* 99(15), 6809-6816. DOI: 10.1016/j.biortech.2008.01.041
- Kongjao, S., Damronglerd, S., and Hunsom, M. (2011). "Electrochemical reforming of an acidic aqueous glycerol solution on Pt electrodes," *Journal of Applied Electrochemistry* 41(2), 215-222. DOI: 10.1007/s10800-010-0226-3
- Kraft, A. (2007). "Doped diamond: A compact review on a new, versatile electrode material," *International Journal of Electrochemical Science*. www.electrochemsci.org/papers/vol2/2050355.pdf
- Kusunoki, Y., Miyazawa, T., Kunimori, K., and Tomishige, K. (2005). "Highly active metal-acid bifunctional catalyst system for hydrogenolysis of glycerol under mild reaction conditions," *Catalysis Communications* 6(10), 645-649. DOI: 10.1016/j.catcom.2005.06.006
- Kwon, Y., Birdja, Y., Spanos, I., Rodriguez, P., and Koper, M. T. M. (2012). "Highly selective electro-oxidation of glycerol to dihydroxyacetone on platinum in the presence of bismuth," *ACS Catalysis* 2(5), 759-764. DOI: 10.1021/cs200599g
- Lee, C. S., Ong, Y. L., Aroua, M. K., and Daud, W. M. A. W. (2013). "Impregnation of palm shell-based activated carbon with sterically hindered amines for CO₂ adsorption," *Chemical Engineering Journal* 219, 558-564. DOI: 10.1016/j.cej.2012.10.064
- Liu, H., Liang, S., Jiang, T., Han, B., and Zhou, Y. (2012). "Hydrogenolysis of glycerol to 1,2-propanediol over Ru–Cu bimetal supported on different supports," *CLEAN – Soil, Air, Water* 40(3), 318-324. DOI: 10.1002/clen.201000227
- Maris, E. P. and Davis, R. J. (2007). "Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts," *Journal of Catalysis* 249(2), 328-337. DOI: 10.1016/j.jcat.2007.05.008
- Markets and Markets. (2016). *Propylene Glycol Market worth \$4.2 Billion by 2019*, Markets and Markets.
- McMorn, P., Roberts, G., and Hutchings, G. J. (1999). "Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts," *Catalysis Letters* 63(3-4), 193-197. DOI: 10.1023/A:1019073122592
- Nakagawa, Y. and Tomishige, K. (2011). "Heterogeneous catalysis of the glycerol hydrogenolysis," *Catalysis Science and Technology* 1(2), 179-190. DOI: 10.1093/COCY00054J
- Omar, S., Girgis, B., and Taha, F. (2003). "Carbonaceous materials from seed hulls for bleaching of vegetable oils," *Food Research International* 36(1), 11-17. DOI: 10.1016/S0963-9969(02)00102-3

- Pandhare, N. N., Pudi, S. M., Biswas, P., and Sinha, S. (2016). "Selective hydrogenolysis of glycerol to 1,2-propanediol over highly active and stable Cu/MgO catalyst in the vapor phase," *Organic Process Research and Development* 20(6), 1059-1067. DOI: 10.1021/acs.oprd.6b00110
- Panizza, M., and Cerisola, G. (2005). "Application of diamond electrodes to electrochemical processes." *Electrochimica Acta*, 51(2), 191-199. DOI: 10.1149/1.1619646
- Qi, J., Xin, L., Chadderdon, D. J., Qiu, Y., Jiang, Y., Benipal, N., Liang, C., and Li, W. (2014). "Electrocatalytic selective oxidation of glycerol to tartronate on Au/C anode catalysts in anion exchange membrane fuel cells with electricity cogeneration," *Applied Catalysis B-Environmental* 154-155, 360-368. DOI: 10.1016/j.apcatb.2014.02.040
- Rode, C. V., Ghalwadkar, A. A., Mane, R. B., Hengne, A. M., Jadkar, S. T., and Biradar, N. S. (2010). "Selective hydrogenolysis of glycerol to 1,2-propanediol: Comparison of batch and continuous process operations," *Organic Process Research and Development* 14(6), 1385-1392. DOI: 10.1021/op1001897
- Roquet, L., Belgsir, E. M., Léger, J. M., and Lamy, C. (1994). "Kinetics and mechanisms of the electrocatalytic oxidation of glycerol as investigated by chromatographic analysis of the reaction products: Potential and pH effects," *Electrochimica Acta* 39(16), 2387-2394. DOI: 10.1016/0013-4686(94)E0190-Y
- Saila, P. and Hunsom, M. (2015). "Effect of additives on one-pot electrochemical conversion of enriched crude glycerol," *Korean Journal of Chemical Engineering*, 1-6. DOI: 10.1007/s11814-015-0066-2
- Sigma Aldrich (2016). (<http://www.sigmaaldrich.com/>), Accessed 1 July 2016.
- Simões, M., Baranton, S., and Coutanceau, C. (2010). "Electro-oxidation of glycerol at Pd based nano-catalysts for an application in alkaline fuel cells for chemicals and energy cogeneration," *Applied Catalysis B: Environmental* 93(3-4), 354-362. DOI: 10.1016/j.apcatb.2009.10.008
- Simões, M., Baranton, S., and Coutanceau, C. (2011). "Enhancement of catalytic properties for glycerol electrooxidation on Pt and Pd nanoparticles induced by Bi surface modification," *Applied Catalysis B: Environmental* 110, 40-49. DOI: 10.1016/j.apcatb.2011.08.020
- Tang, J., Wang, T., Sun, X., Hu, Y., Xie, Q., Guo, Y., Xue, H., and He, J. (2013). "Novel synthesis of reduced graphene oxide-ordered mesoporous carbon composites and their application in electrocatalysis," *Electrochimica Acta* 90, 53-62. DOI: 10.1016/j.electacta.2012.11.099
- Valencia, R., Tirado, J. A., Sotelo, R., Trejo, F., and Lartundo, L. (2015). "Synthesis of 1,2-propanediol through glycerol hydrogenolysis on Cu–Al mixed oxides," *Reaction Kinetics, Mechanisms and Catalysis* 116(1), 205-222. DOI: 10.1007/s11144-015-0885-5
- Vasiliadou, E. S., and Lemonidou, A. A. (2011). "Parameters affecting the formation of 1,2-propanediol from glycerol over Ru/SiO₂ catalyst," *Organic Process Research and Development* 15(4), 925-931. DOI: 10.1021/op2000173
- Wołosiak-Hnat, A., Milchert, E., and Lewandowski, G. (2013). "Optimization of hydrogenolysis of glycerol to 1,2-propanediol," *Organic Process Research and Development* 17(4), 701-713. DOI: 10.1021/op4000175
- Xia, S., Yuan, Z., Wang, L., Chen, P., and Hou, Z. (2012). "Catalytic production of 1,2-propanediol from glycerol in bio-ethanol solvent," *Bioresource Technology* 104, 814-

817. DOI: 10.1016/j.biortech.2011.11.031
- Xia, S., Zheng, L., Wang, L., Chen, P., and Hou, Z. (2013). "Hydrogen-free synthesis of 1,2-propanediol from glycerol over Cu-Mg-Al catalysts," *RSC Advances* 3(37), 16569-16576. DOI: 10.1039/C3RA42543F
- Yadav, G. D., Chandan, P. A., and Tekale, D. P. (2012). "Hydrogenolysis of glycerol to 1,2-propanediol over nano-fibrous Ag-OMS-2 catalysts," *Industrial and Engineering Chemistry Research* 51(4), 1549-1562. DOI: 10.1021/ie200446y
- Yildiz, G. and Kadirgan, F. (1994). "Electrocatalytic oxidation of glycerol: I. Behavior of palladium electrode in alkaline medium," *Journal of The Electrochemical Society*, 141(3), 725-730. DOI: 10.1149/1.2054799
- Yuan, Z., Wang, J., Wang, L., Xie, W., Chen, P., Hou, Z., and Zheng, X. (2010). "Biodiesel derived glycerol hydrogenolysis to 1,2-propanediol on Cu/MgO catalysts," *Bioresource Technology* 101(18), 7088-7092. DOI: 10.1016/j.biortech.2010.04.016
- Zhang, Z., Xin, L., Qi, J., Chadderton, D. J., Sun, K., Warsko, K. M., and Li, W. (2014). "Selective electro-oxidation of glycerol to tartronate or mesoxalate on Au nanoparticle catalyst via electrode potential tuning in anion-exchange membrane electro-catalytic flow reactor," *Applied Catalysis B: Environmental* 147, 871-878. DOI: 10.1016/j.apcatb.2013.10.018

Article submitted: 12 July 2017; Peer review completed: September 24, 2017; Revised version received and accepted: October 21, 2017; Published: November 6, 2017.
DOI: 10.15376/biores.13.1.115-130