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Highly selective transformation of glycerol to dihydroxyacetone without using oxidants by PtSb/C-catalyzed electrooxidation process

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We demonstrate an electrocatalytic reactor system for the partial oxidation of glycerol in an acidic solution to produce value-added chemicals, such as dihydroxyacetone (DHA), glyceraldehyde (GAD), glyceric acid (GLA), and glycolic acid (GCA). Under optimized conditions, the carbon-supported bimetallic PtSb (PtSb/C) catalyst was identified as a highly active catalyst for the selective oxidation of glycerol in the electrocatalytic reactor. The product selectivity can be strongly controlled as a function of the applied electrode potential and catalyst surface composition. The main product from the electrocatalytic oxidation of glycerol was DHA, with a yield of 61.4% of DHA at a glycerol conversion of 90.3%, which can be achieved even without using any oxidants over the PtSb/C catalyst at 0.797 V (vs. SHE, standard hydrogen electrode). The electrocatalytic oxidation of biomass-derived glycerol represents a promising method of chemical transformation to produce value-added molecules.

Introduction

Biomass feedstocks are alternative sources of valued chemicals in place of fossil fuels.^{1–3} Glycerol can be obtained as a byproduct during the production of biodiesel from biomass. Biomass-derived glycerol is an attractive source of valuable chemicals and chemical building blocks for the synthesis of fine chemicals from renewable sources.^{3–5} The oxidation of glycerol produces various chemicals, such as dihydroxyacetone (DHA), glyceraldehyde (GAD), glyceric acid (GLA), hydroxypyruvic acid (HPA), tartronic acid (TTA), glycolic acid (GCA), and oxalic acid (OXA).^{6–9} In particular, dehydrogenative oxidation of glycerol can lead to the production of DHA, which is a potentially important chemical that is used as a main ingredient in the cosmetic industry and as building blocks of new degradable polymers.^{10–13}

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intermediates has been previously investigated using heterogeneous catalysis via conventional catalytic processes with various catalysts, such as Pd,¹³⁻¹⁶ Au,^{13-15,17,18} Pt,^{15,16,19} PtBi,^{11,20-23} PtPd,²⁴ PtAu,^{25,26} AuPd,^{27,28} Au-Pt/H-mordenite,²⁹ and Pt/MWCNTS.³⁰ The electrochemical conversion process by tuning the applied potential has also been used to convert intermediate products using the electrocatalytic oxidation of glycerol.^{31–35} The electrocatalytic oxidation process can control the oxidizing conditions by variation in the electrode potential, which can alter the reaction rate and product selectivity.^{34,36} Scheme 1 represents the dehydrogenative oxidation of biomass-derived glycerol in an electrocatalytic reactor system. The dehydrogenation of glycerol generates DHA, protons, and electrons over the anode electrode (i.e., working electrode, WE) in this electrocatalytic reactor. At the cathode (i.e., counter electrode, CE), the protons in the electrolyte solution combine with the electrons transported from the anode to form dihydrogen gas. The reactions involved in this process are as follows:

The oxidation of glycerol to valued chemicals or

Anode reaction (working electrode): $C_3H_8O_3 \rightarrow C_3H_6O_3 + 2H^{+}_{(aq)} + 2e^{-}$ Cathode reaction (counter electrode): $2H^{+}_{(aq)} + 2e^{-} \rightarrow H_2$ Overall reaction: $C_3H_8O_3 \rightarrow C_3H_6O_3 + H_2$

A recent study reported the selective electrocatalytic glycerol oxidation of GLA (45%) and TTA (38%) at a glycerol conversion of 20.4% on a Pt/C catalyst using an anion-exchange membrane fuel cell reactor.³² Wang et al. demonstrated the high selectivity of glycerol electrocatalytic oxidation to glyceric acid over gold-based catalysts supported on poly(4-

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Scheme 1 Schematic illustration of the dehydrogenative oxidation of biomassderived glycerol in an electrocatalytic reactor system.

vinylpyridine)-functionalized graphene (Au-P4P/G).³³ Ciriminna et al. reported electrocatalytic glycerol oxidation mediated by the TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) oxidant with DHA and HPA yields of 30% and 35%, respectively after 200 h.¹² Moreover, the highly selective formation of DHA can be achieved by electrooxidation of glycerol using a Pt/C electrode in the presence of bismuth dissolved in an electrolytic solution.³⁵ Currently, Pt-Bi nanoparticles are considered to be a good candidate for electrocatalysts for DHA formation, which requires oxidative dehydrogenation of glycerol. However, this process exhibited relatively lower selectivity and glycerol conversion. The PtSb nanoparticles can enhance the oxidative dehydrogenation of glycerol and hinder further oxidation of intermediates.^{37,38} Despite of these advantages, PtSb catalyst systems using electrochemical methods have not been previously explored with thorough characterization of the selective oxidation of glycerol under acidic conditions.

In this study, carbon-supported bimetallic PtSb (PtSb/C) was applied as an active and stable electrocatalyst for the dehydrogenation of glycerol in an electrocatalytic reactor to investigate the electrode potential-dependent product distribution and yield. A high yield of DHA (61.4% at 90.3% conversion) can be obtained over the PtSb/C catalyst at 0.797 V (vs. SHE, standard hydrogen electrode) under acidic condition. The synergistic effect of the alloyed Pt–Sb catalyst for DHA production was demonstrated using electrochemical methods and discussed in terms of the proposed reaction pathway and physicochemical properties of the bimetallic nanoparticles.

Experimental

Materials

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Hydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆•xH₂O, Aldrich), bismuth(III) chloride (BiCl₃, Aldrich), and antimony(III) chloride (SbCl₃, Aldrich) were used as the metal precursors for the catalysts. Vulcan XC-72R carbon powder (Cabot Corp., S_{BET} = 236.8 m² g⁻¹) was used as the supporting material for the PtBi and PtSb nanoparticles, and the carbon powder was pretreated with 6 M hydrochloric acid (HCl, 37%) prior to use. Tetraethylene glycol ($C_4H_{10}O_3$, Sigma-Aldrich) was used as the reductant and stabilizer to produce PtBi and PtSb nanoparticle catalysts. The chemicals used in the reactant solutions and standards included glycerol ($C_3H_8O_3$, 99.5% Junsei), dihydroxyacetone ($C_3H_6O_3$, 97% Aldrich), glyceraldehyde ($C_3H_6O_3$, 99.5% Fisher), glyceric acid ($C_3H_6O_4$, 99.5% Fisher), hydroxypyruvic acid ($C_3H_4O_4$, 95% Sigma-Aldrich), tartronic acid ($C_3H_4O_5$, 97% Fluka), glycolic acid ($C_2H_4O_3$, 97% Fluka), and oxalic acid ($C_2H_2O_4$, 98% Aldrich).

Synthesis of carbon-supported PtBi and PtSb catalysts

The carbon-supported 40 wt% PtBi and PtSb catalysts were synthesized using a colloidal method that was modified from a previously reported method.39 The carbon support was activated in an acid solution consisting of 6 M hydrochloric acid (HCl, 37%) for 12 h. Then, the pretreated carbon was washed several times with deionized (DI) water until the solution pH was approximately 5.5 followed by filtering and drying for 5 h in air at 393 K. The activated carbon was ultrasonically dispersed in 40 ml of tetraethylene glycol with a sodium hydroxide solution (NaOH, 50% solution in water) until the solution pH was approximately 9. In a typical synthesis reaction, the calculated amount of Pt salt was completely dissolved in the carbon-suspended solution with vigorous stirring. The solutions were heat-treated to produce Pt colloids by heating at 433 K for 2 h with stirring under reflux condition followed by cooling to room temperature. The resulting slurries were filtered and rinsed thoroughly with DI water and then vacuum-dried via a freeze-drying method. To prepare the PtBi/C and PtSb/C catalysts, the precalculated amounts of Bi or Sb salt were added to the Pt/C-suspended tetraethylene glycol solution at a pH of 9. Then, the solution was heated at 523 K for 2 h with stirring using a reflux system. The final solution was filtered, washed, and dried under vacuum via a freezedrying method to minimize particle agglomeration for the highly dispersed nanoparticle catalysts. Finally, the dried Pt/C, PtBi/C, and PtSb/C catalysts were heat-treated under an H₂ atmosphere at 373 K for 1 h.

Physicochemical characterizations of the PtBi/C and PtSb/C catalysts

The prepared catalysts were characterized by various physicochemical analyses, such as transmission electron microscopy (TEM) and X-ray diffraction (XRD) to investigate the structural modification, energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the chemical properties, and X-ray photoelectron spectroscopy (XPS) and Xabsorption-near-edge spectroscopy (XANES) ray to characterize the electronic features of the bimetallic catalysts. The XRD measurements were performed with a Rigaku Rotalflex (RU-200B) diffractometer using a Cu K α (λ = 1.5418 Å) source and a Ni filter to characterize the structural changes in the Pt-based crystallites. The source was operated at 40 kV and 100 mA. The 20 angular region between 10° and 80° was explored using a fixed time mode (0.025°/3 s). The Pt, PtBi and PtSb nanoparticle morphologies on the carbon support were examined using a TECHNAI- F20 TEM operated at 200 kV. All of the TEM samples were prepared by ultrasonically dispersing the catalyst particles in an ethanol solution. Drops of the suspension were placed onto a standard Cu grid (200-mesh) that was covered with a carbon film and dried for 30 min in a convection oven to evaporate the ethanol and leave the catalyst particles dispersed on the grid prior to being inserted into the microscope. ICP-AES analyses were performed using an OPTIMA 4300 DV (PerkinElmer, USA) to estimate the actual metal loading and the chemical composition of the carbon supported Pt, PtBi and PtSb catalysts. An EDS analysis was also performed to determine the purity and chemical dispersion of the PtBi and PtSb nanoparticles at 200 kV using an INCA-X (Oxford Instruments) in conjunction with TEM. The surface oxidation states of the Pt, PtBi, and PtSb catalyst were analyzed by XPS (ESCALAB 250, UK) using a monochromic Al Ka X-ray source (E = 1486.6 eV). The background was corrected using the Shirley method, and the binding energy (BE) of the C 1s peak from the support at 284.5 eV was used as an internal standard. Data processing was performed with the XPSPEAK software program. The Pt:Bi (or Sb) surface atomic ratios were calculated from peak areas that were normalized by the published atomic sensitivity factor of the corresponding element.⁴⁰ XANES was performed at beam lines 3C1 and 7C at the Pohang Accelerator Laboratory (PAL; 2.5 GeV with the stored currents of 130-180 mA), Korea. A Si (1 1 1) double crystal monochromator was used to monochromatize the Xray photon energy. The spectra were obtained at room temperature in transmission mode for the L3-edge of Pt (11,564 eV) under ambient conditions. Higher-order harmonic contamination was eliminated bv detuning the monochromator to reduce the incident X-ray intensity by approximately 30%. Energy calibration was performed using a standard metal foil. XANES was analyzed using the IFEFFIT software program.^{41,42} Then, the resulting elemental absorption was normalized using the atomic-like absorption at the edge. The white line (WL) areas of the Pt L₃-edge were calculated by adopting an arctangent step and fitting a Lorentzian function to the WL curve in the region from 50 to 100 eV.

Oxidation reaction of glycerol in an electrocatalytic reactor

Electrooxidation of glycerol was carried out in an electrocatalytic three-electrode reactor using a potentiostat (Solartron Analytical 1400, AMETEK) to control the electrode potential. A Pt wire and Ag/AgCl (in 3 M KCl) were used as the counter and reference electrodes, respectively. A carbon paper (Toray, TGP-H090) was used as the working electrode for the glycerol electrooxidation reaction. For the catalyst-coated carbon paper, the prepared Pt/C, PtBi/C, and PtSb/C catalysts were suspended in isopropyl alcohol, which contained a 5 wt% Nafion solution (DuPont), for 3 h by sonication. Next, catalyst ink was deposited on the surface of the carbon paper electrodes (with a 2 cm² geometric area and

 0.2 mg cm^{-2} metal loading) using a spray method followed by drying in an oven at 343 K for 1 h to prepare a thin film of catalyst impregnated on the vitreous carbon electrode for use as the working electrode. Oxidation of glycerol was carried out in a 10 ml mixture consisting of 0.1 M glycerol in a 0.5 M H₂SO₄ solution with stirring at 400 rpm. The temperature was controlled by directly heating the electrochemical reactor using a temperature regulator. Prior to any electrochemical measurements, the mixture was completely purged with pure N₂ to eliminate the dissolved dioxygen gas. The pH values of the mixture were nearly the same during the reaction and invariant under all of the conditions with a pH variation of 0.4-0.6. The turnover frequency (TOF) was determined at conversions of less than 10%. From the cyclic voltammograms (CVs) (See Fig. S1 in ESI⁺), the electrochemical active surface areas (EAS) values were estimated from the oxidation charges of the surface Pt-H species (210 μ C cm⁻²).³⁹ EAS of the Pt/C, PtBi/C, and PtSb/C electrodes was measured as 43.9, 30.5,

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H₂SO₄. The reaction products formed during glycerol electrooxidation were collected and examined by analyzing each phase of the reaction mixture using high-performance liquid chromatography (HPLC, Waters 2535) with a RI detector and UV-Vis detector (220 nm). A Biorad Aminex HPX-87H sugar column was used with 0.005 M H₂SO₄ (at a flow rate of 0.6 ml min⁻¹) as the eluent at 65 °C. 1 μ l liquid samples were injected after filtration through a 0.2 µm filter. The amount of consumed glycerol and the reaction product yields were quantified with an external calibration method. The glycerol conversion (X_{Glv}), product selectivity (S_p), and reaction rate (R) were calculated according to the C2 and C3 products present in the liquid phase, where n is the moles of compound and in/out is the reactor inlet/outlet. All of the reaction rates were calculated at glycerol conversions of less than 10%.

31.3 $m^2 g_{-Pt}^{-1}$, respectively. These measurements were taken

using the cyclic voltammetry data recorded in the 0-1.2 V

potential range (vs. SHE) at a 50 mV s⁻¹ scan rate in 0.5 M

$$X_{Gly} (\%) = \frac{n_{Gly,in} - n_{Gly,out}}{n_{Gly,in}} \times 100$$
$$S_p (\%) = \frac{n_{p,out}}{n_{Gly,in} - n_{Gly,out}} \times 100$$

$$R\left(mol_{Gly}mol_{Pt}^{-1}min^{-1}\right) = \frac{n_{Gly,in} - n_{Gly,out}}{n_{Pt} \times t}$$

Results and discussion

Characterization of the PtBi/C and PtSb/C catalysts

Fig. 1 shows representative TEM images with particle size distributions for the Pt/C, PtBi/C, and PtSb/C catalysts. All of the prepared metal nanoparticles were highly dispersed and uniformly deposited on the carbon support. The mathematical mean particle diameter (*d*) was calculated using the following equation:

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Fig. 1 TEM images of the Pt/C, PtBi/C, and PtSb/C catalysts with EDS spectra and particle size distributions for the metal nanoparticles

$$d = \frac{\sum n_i d_i}{\sum n_i}$$

where n_i is the frequency of the catalyst particles with a diameter of size d_i . The mean particle size of the PtBi/C and PtSb/C catalysts was approximately 4.2-4.3 nm, which would be slightly larger than that of Pt/C (ca. 3.6 ± 0.9 nm), as listed in Table 1.

The metal loadings of Pt, PtBi, and PtSb over the carbon supports determined by ICP-AES were ca. 39.1, 39.7 and 38.4 wt%, respectively, as summarized in Table 1. These values are close to the pre-calculated value of 40 wt% during the preparation. The results from the ICP-AES indicate that the bulk atomic ratios are 89.9:10.1 for Pt:Bi and 90.1:9.9 for

Table 1 Quantitative composition and structural parameters for the Pt/C, PtBi/C
and PtSb/C catalysts measured using ICP-AES, TEM, and XRD

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	Metal loading ^a (wt%)		Mean particle size (nm)		$2\theta_{max}^{d}$	Lattice parameter ^e
Catalysts	Pt	Bi, Sb	TEM ^b	XRD^{c}	(°)	(Å)
Pt/C	39.1	-	3.6 ± 0.9	4.3	67.53	3.920
PtBi/C	35.4	4.26	4.3 ± 1.2	4.8	67.07	3.944
PtSb/C	35.9	2.47	4.2 ± 0.9	4.6	67.17	3.938

^a Metal loading amounts on the carbon support estimated from ICP-AES analysis. ^b Mean particle diameter of the catalysts from TEM images using at least 200 visible particles. ^c Crystallite sizes of the catalysts calculated by line broadening of powder XRD peak. ^d The angular position of Pt (2 2 0) reflection peak.^e Lattice parameter calculated from XRD analysis.

Pt:Sb, which are nearly consistent with the nominal atomic ratio (90:10). This result is also confirmed by the results from the EDS analysis (i.e., 87:13 for Pt:Bi, 92:8 for Pt:Sb) that are shown in Fig. 1. No impurities, such as Cl, were observed in the synthesized catalysts based on EDS.

The XRD patterns of the Pt/C, PtBi/C, and PtSb/C catalysts are shown in Fig. 2(a). The first broad peak located at approximately 25° was due to the (0 0 2) plane in the hexagonal structure of the Vulcan XC-72R carbon black support.⁴³ The main characteristic peaks at approximately 39°, 46°, and 67°, which appeared in all of the catalysts, correspond to the (1 1 1), (2 0 0), and (2 2 0) planes, respectively, of a crystalline face-centered cubic (fcc) Pt phase. It is important to note that any noticeable characteristic peaks from the Bi and Sb metal phases, their metal oxides/hydroxides, or other compounds were not detected in the XRD measurements, which implies that these secondary phases may only be present in very small amounts or in amorphous forms in the prepared materials.^{37,44} The lattice parameters and mean particle size of the prepared catalysts were calculated according to the angular position $(2\vartheta_{max})$ of the (2 2 0) peaks and the full width at half maximum (FWHM), as summarized in Table 1. The shifts in the 2ϑ position from the Pt crystallites and corresponding changes in their lattice parameters reflect the incorporation of either Bi or Sb atoms into the Pt crystal lattice. In this study, the Pt (2 2 0) reflection peak from PtBi/C and PtSb/C appears to be slightly shifted toward a lower 20 value compared to that from Pt/C, indicating increases in the lattice parameter with lattice dilation when either Sb or Bi

Table 2 Electronic parameters and chemical composition of the catalysts characterized by XPS, XANES, and ICP-AES measurements								
	Binding energy (eV)		Pt/M (atomic r	Pt/M (atomic ratio)		XANES		
Catalysts	Pt 4f _{7/2}	Bi 4f _{7/2} , Sb 3d _{5/2}	From ICP ^d	From XPS ^e	$E_0 (eV)^f$	WL intensity (a.u.) ^g		
Pt foil	-				11564.3	1.22		
Pt/C	71.27 (63) ^a	-	-	-	11564.7	1.39		
	72.44 (37) ^a	-						
PtBi/C	71.60 (66)	158.1 (65) ^b	8.9	3.1	11564.4	1.44		
	72.79 (34)	159.3 (35) ^b						
PtSb/C	71.62 (72)	529.5 (73) ^c	9.1	4.5	11564.0	1.41		
	72.90 (28)	530.5 (27) ^c						

^a Relative % of the Pt⁰ and Pt²⁺ species. ^b Relative % of the Bi⁰ and Bi²⁺ species. ^c Relative % of the Sb⁰ and Sb³⁺ species. ^d Chemical composition determined by ICP-AES analysis. ^e Surface atomic ratio calculated from XPS by using peak areas normalized on the basis of sensitivity factors. ^f Pt L₃-edge energy. ^g White line intensity.

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Fig. 2 (a) X-ray diffraction patterns, (b) X-ray photoelectron spectra of Pt 4*f*, Bi 4*f*, and Sb 3*d*, and (c) Pt L₃ edge XANES spectra along with Pt foil as the reference for the Pt/C, PtBi/C, and PtSb/C catalysts.

atoms are incorporated into the fcc lattice of the Pt crystallites.^{37,45,46} The calculated crystallite sizes for the Pt, PtBi, and PtSb particles on carbon were approximately 4.3, 4.8, and 4.6 nm, respectively.

Based on the XRD and TEM measurements, no significant differences were observed in the metal particle size under our preparation conditions. Therefore, the particle size effects does not influence the electrocatalytic activity and selectivity over PtBi/C and PtSb/C.

XPS measurements were carried out to elucidate the surface oxidation states of the synthesized catalysts. Fig. 2(b) shows the XPS spectra for Pt 4f, Bi 4f, and Sb 3d in the carbon supported Pt, PtBi, and PtSb catalysts. The binding energy (eV) of the core electrons and relative chemical states for Pt 4f, Bi 4f, and Sb 3d were estimated from the relative intensities of their deconvoluted peaks (Table 2). The Pt 4f XPS spectra contained two peaks corresponding to the Pt $4f_{7/2}$ and $4f_{5/2}$ states from the spin-orbital splitting, and each peak can be deconvoluted to two different Pt oxidation states (i.e., Pt⁰ and $\mathsf{Pt}^{2*}).^{37,38}$ The two peaks located near 71 eV and 72 eV may be due to zero-valent Pt and Pt²⁺, respectively, and the latter peak may be produced from the surface layer formation with Pt- $O_{(ad)}$ bonds.^{47,48} Pt⁰ is a predominant species (60~70% in amount) in all of the prepared catalysts with relatively small amounts of oxidized Pt species (30~40%). The Pt 4f binding energies for PtBi/C (71.60 eV) and PtSb/C (71.62 eV) were shifted to higher levels compared to that of the Pt/C (71.27 eV) catalyst, which implies that the electronic state of Pt was modified by the addition of Bi or Sb.^{37,44} The Bi 4f spectra was

deconvoluted into two pairs of peaks at 158.1 eV, which were assigned to Bi⁰ (65%) and 159.3 eV assigned to Bi²⁺ (35%). For Sb 3d XPS, the Sb $3d_{5/2}$ spectra were also deconvoluted into two distinguishable peaks with different intensities, and these peaks correspond to Sb^{0} and Sb^{3+} . Approximately 73% and 27% of surface antimony exist as Sb⁰ and Sb³⁺, respectively, in the PtSb/C catalyst. The Sb 3d_{5/2} spectrum contained an overlapping peak with high binding energy, which is the O 1s oxygen peak at 531.9 eV.^{37,48} The results from the XPS investigation suggest that the dominant surface phases for Bi and Sb in the PtBi/C and PtSb/C consist of zero-valent species. In Table 2, the Pt/M atomic ratios for the PtBi/C or PtSb/C catalysts measured by XPS were lower than those measured using ICP-AES, which suggests that either Bi or Sb was relatively enriched at the surface layer of the PtBi/C and PtSb/C catalysts, which is consistent with results that were reported elsewhere.^{22,23}

For the electronic structure analysis of these catalysts, the XANES spectra for the Pt L₃ edges of the prepared catalysts were obtained and are shown in Fig. 2(c), and the fitted parameters are listed in Table 2. Overall, the XANES shapes of PtBi/C and PtSb/C are similar to those of Pt foil and Pt/C except for the edge absorption intensity. The strong peak above the edge energy position (see the magnified region in the inset figure) is closely related to the density of the vacant 5*d* electronic states of Pt.⁴⁹ This white line (WL) peak is frequently recognized as an important parameter for catalytic activity.⁵⁰ The WL intensities of both the PtBi/C and PtSb/C catalysts are slightly higher than that of Pt/C, which may be

due to a decrease in 5*d* orbital filling in the Pt alloys due to oxidation and hybridization. With respect to the Sb content, the relationship between the physicochemical properties and the electrocatalytic activities will be explored and discussed for glycerol electrooxidation.

Selective oxidation of glycerol via an electrochemical reaction

Glycerol oxidation was performed over the Pt-based catalyst in an electrocatalytic reactor using a solution consisting of 0.1 M glycerol in a 0.5 M H₂SO₄ electrolyte at 60 °C at a constant potential of 0.797 V (vs. SHE). The oxidation of glycerol produced several products including DHA, GAD, GLA, HPA, TTA, GCA, and OXA.⁶⁻⁹ Fig. 3(a) shows the DHA, GAD, and GLA product distributions at a glycerol conversion of 50% on the (a) Pt/C, (b) PtBi/C, and (c) PtSb/C catalysts. For Pt/C, GAD and GLA were primarily observed during glycerol oxidation, while the selectivity to DHA was only 2% or less. For PtBi/C, DHA formation was more favorable. However, a smaller amount of GAD was observed compared to the results for Pt/C. For PtSb/C, the selectivity to DHA was as high as 80% with a DHA/GAD selectivity ratio of approximately 8. The difference in the product distributions may be attributed to the different structural and electronic properties of the Pt/C, PtSb/C, and PtBi/C catalysts. The negligible activity for glycerol oxidation over Bi/C and Sb/C (See Fig. S2 in ESI⁺) indicates that Bi or Sb alone was not capable of activating the chemical reactions with glycerol. The product selectivity is reported as a function of glycerol conversion for the PtSb/C catalyst in Fig. 3(b). When



Fig. 3 (a) Selectivity to DHA, GAD, and GLA at a glycerol conversion of 50% over the Pt/C, PtBi/C, and PtSb/C catalysts and (b) glycerol conversion as a function of the product selectivity over the PtSb/C catalysts. [Feed solution: 0.1 M glycerol; Anode applied potential: 0.797 V; Reaction temperature: 60 °C]





the glycerol conversion was 10%, DHA was the main product with nearly 100% selectivity, while GAD and GLA were barely observed. As the glycerol conversion increased, the DHA selectivity slightly decreased, which most likely indicates that DHA was an intermediate product during glycerol oxidation. When the glycerol conversion increased to 90%, the selectivity to GAD and GLA increased to 18.7% and 7.9%, respectively, and the selectivity to DHA decreased to 68.1%. However, DHA remained the predominant product with high selectivity at all glycerol conversions.

Fig. 4 shows the DHA yield and initial reaction rate at conversions less than 10% for the oxidation reaction of glycerol. A high DHA yield (61.4%) and reaction rate (4.6 $mol_{glycerol} mol_{Pt}^{-1} min^{-1}$) were achieved with the PtSb/C catalyst system. The DHA yield decreased in the following order: PtSb/C > PtBi/C > Pt/C. The PtSb/C catalyst exhibited a higher DHA yield, which was 38 times higher than that of the Pt/C catalyst. The initial reaction rate decreased as follows: PtSb/C > Pt/C ~ PtBi/C. The initial reaction rate of the PtSb/C catalyst was 63% higher than that of the PtBi/C catalyst for the oxidation of glycerol. The different reactivities with the catalysts may be explained by the CV results (see Fig. S3 in ESI⁺). The CV curves exhibit two typical anodic peaks due to the electrooxidation of glycerol molecules. The forward anodic peak current density (i_f) was due to the oxidation currents for breaking the C-H or C-C bonds during glycerol electrooxidation. The reverse anodic peak current density (i,) was due to the oxidation currents for removal of the incompletely oxidized carbonaceous residues on the Pt surface. The i_f/i_r ratio for the PtSb/C catalyst was larger than those for Pt/C and PtBi/C, which indicates a lower accumulation of intermediate residues on the catalyst during the glycerol electrooxidation processes. The carbonaceous intermediates tend to strongly adsorb on the Pt surface, which can block the active catalyst sites for the next turnover making the oxidation reactions more sluggish.^{47,51}

Various reaction parameters (i.e., applied potentials, reaction temperature, and reaction time) were investigated over the PtSb/C catalyst. The glycerol conversion, DHA selectivity, and reaction rate as a function of increasing applied potential are compared in Fig. 5(a). As the applied potential

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Fig. 5 Performance of the PtSb/C catalysts in the electrooxidation of glycerol as a function of the (a) applied electrode potential and (b) reaction temperature. [Reaction conditions: (a) 0.1 M glycerol, 60 °C, 10 h; (b) 0.1 M glycerol, 0.797 V, 10 h]

increased, the glycerol conversion increased to 95.8% up to 0.997 V but then slightly decreased at higher potentials. The DHA selectivity and reaction rate increased from 0.397 V to 0.797 V but then decreased when the applied potential increased to 1.197 V. At an applied potential of 0.797 V, the DHA selectivity increased to 68%., while at 1.197 V, its selectivity was only 35.4%. At higher potentials, the C-C bond cleavage reaction dominated, resulting in lower selectivity to DHA. This result will be further discussed below and supported by the DHA selectivity being strongly dependent on the applied potential (Fig. 6). The temperature effect was explored in a temperature range of 25 °C to 70 °C. The reaction temperature can change the activation barrier for glycerol oxidation, which can affect the reaction rate and product selectivity.²⁰ As shown in Fig. 5(b), the conversion of glycerol increased from 20% to 95.8% from 25 °C to 70 °C, and the reaction rate also proportionally increased from 1.0 to 5.0 mol_{glycerol} mol_{Pt}⁻¹ min⁻¹. These results indicate that an increase in temperature can directly promote the glycerol electrooxidation reaction. The reaction rate appears to be significantly affected by temperature under the studied reaction conditions. No significant changes in the DHA selectivity were observed for the studied temperature range. The kinetic information as well as the apparent activation energy (E_a) from the experimental results are shown in Fig. S4. Further experimental studies are required to establish the rate-determining steps (rds) and calculate the theoretical E_a. The increasing applied potential and reaction temperature can increase the activity with a high

current density (See Fig. S5 in ESI⁺) because these parameters modify the activation energy required to cleave the C–C bond and oxidatively remove the carbonaceous species adsorbed on the Pt sites for glycerol oxidation.

The time-dependent glycerol conversion and product distribution on PtSb/C catalysts are compared in Fig. S6. As expected in the batch-type reactor, the glycerol conversion increased gradually with the reaction time. At a reaction time of 0.5 h, the DHA selectivity reached a maximum and gradually decreased with reaction time, which may be due to the subsequent oxidations of DHA under the reaction conditions. DHA exhibited the highest selectivity at all of the glycerol conversions compared to the other products. The GAD selectivity was less than 20% and remained nearly constant after 2 h. The GAD was the primarily observed product over Pt/C and PtBi/C compared to that over PtSb/C under these conditions, indicating that the dehydrogenative oxidation of glycerol to DHA was more favorable on the PtSb/C surface at 0.797 V. The minor products (i.e., HPA and TTA) were observed after 8 h. However, the expected C₂ intermediates, such as GCA and OXA, were not observed, which may be due to the oxidation of the C₃ to C₂ molecules accompanied by C-C bond cleavage being hindered over PtSb/C under this reaction condition.

The influence of the applied potential on the product distributions for the conversion of glycerol over the Pt/C, PtBi/C, and PtSb/C catalysts was investigated, and the results are shown in Fig. 6. On the Pt/C catalyst, as the applied potential increased from 0.397 V to 1.197 V, the GAD selectivity decreased, and GLA selectivity gradually increased, while the selectivity to DHA was less than 5% for all of the potential ranges. For PtBi/C, DHA formation is more favorable compared to that on Pt/C, which is in agreement with previous results using PtBi electrocatalysts by Kimura et al.^{22,23} It is important to note that the DHA selectivity decreased dramatically from 0.597 V because the Bi on the Pt surface forms Bi oxide/hydroxide species at 0.6-0.7 V, which are not active for this reaction.^{35,38,52} For PtSb/C, at lower potentials. observations similar to PtBi/C were made. As the applied potential increased, the glycerol conversion increased from 22.5% to 92.7%. The selectivity of DHA increased from 57.6% to 68.1% with potentials ranging from 0.397 V to 0.797 V. However, the selectivity of GAD and GLA gradually decreased from 0.397 V to 0.797 V and then increased to 1.197 V. The minor products from glycerol oxidation (i.e., HPA, TTA, GCA, and OXA) appeared to form at high potentials via consecutive oxidations of GLA, indicating that a higher applied potential may facilitate C-C bond cleavage as well as C-H and O-H bond breakage.^{32,33} These differences in product distribution among the tested catalysts indicate that the reaction pathway of glycerol electrocatalytic oxidation is strongly dependent on the nature of the catalyst and the electrode potential. The carbon balance of the reaction products was examined on the detected C_2 and C_3 -type products that were present in the liquid phase (see Table S1 in ESI⁺). The carbon balance tended to decrease as the applied potential increased from 0.397 V to 1.197 V, which indicates that more C_2 products (e.g., GCA and ARTICLE

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Fig. 6 Product distribution and glycerol conversion with different applied potentials over the (a) Pt/C, (b) PtBi/C, and (c) PtSb/C catalysts. [Reaction conditions: 0.1 M glycerol, 60 °C, 10 h]

OXA) were further oxidized into C₁ molecules (e.g., formic acid and carbon dioxide) due to the high electrode potential facilitating C-C bond cleavage. At 0.797 V, the carbon balance for Pt/C and PtSb/C was 83.0% and 97.9%, respectively. This result indicates that more products were oxidized to C1 products (formic acid and carbon dioxide) over Pt/C compared to that over the PtSb/C catalysts and the bimetallic PtSb/C system could be advantageous for selective glycerol oxidation reactions.

Glycerol oxidation to valued chemicals or intermediates has been studied over various catalysts using O_2 as an oxidant. For example, Nie et al. reported the production of DHA (46.3% yield) over PtSb alloy catalysts under base-free conditions using O_2 oxidant (glycerol/Pt molar ratio = 557).³⁸ In our electrocatalytic process, the yield of DHA was 61.4% at a glycerol conversion of 90.3% (glycerol/Pt molar ratio = 617), which is approximately 32% higher than that obtained with the non-electrocatalytic system. The TOF of this electrocatalytic system (843.0 h^{-1}) was comparable to that of the nonelectrocatalytic system (878.1 h⁻¹). The electrocatalytic oxidation process of glycerol possesses several key advantages over the catalytic oxidation processes of glycerol including



Fig. 7 Stability test of the PtSb/C electrode for glycerol oxidation. [Reaction conditions: 0.1 M glycerol, 0.797 V, 60 °C, 10 h]

control of the activation barrier by tuning the applied electrode potential.^{34,35} Another advantage is that a strong oxidant, such as O₂, is not required.

To investigate the electrocatalytic stability of PtSb/C for selective glycerol oxidation, recycling experiments were carried out, as shown in the Fig. 7. These results were obtained from repeated cycles in a mixture of 0.1 M glycerol and 0.5 M H₂SO₄ at a constant potential of 0.797 V (vs. SHE). The electrode was washed several times with DI water and then dried in an oven at 343 K for 2 h prior to reuse. The glycerol conversion and selectivity to DHA and GAD were retained with only ~ 5% variations during the 5 cycles of repeated reactions.

Effects of Sb in the PtSb/C on the selective glycerol oxidation

The atomic ratios of Pt/Sb in the PtSb/C catalysts exhibited lower values based on measurements using the surfacespecific XPS technique compared to those quantified using ICP for the bulk compositions (See Table 2). These compositional analyses indicate that the Sb element is relatively enriched in the surface layer of the bimetallic Pt alloy catalysts. From the CVs of the Pt/C, PtBi/C, and PtSb/C catalysts (See Fig. S1 in ESI⁺), which were performed in a 0.5 M H₂SO₄ electrolyte at a 50 mV s⁻¹ scan rate between 0 and 1.2 V (vs. SHE) without glycerol, Pt/C exhibited a high oxygen-reduction peak at approximately 0.74 V during the cathodic scan, while the reduction peak for the PtBi/C and PtSb/C catalysts appeared to be smaller. Additionally, the adsorption and desorption peaks with hydrogen were broader and smaller for the PtBi/C and PtSb/C catalysts but Pt/C exhibited the well-defined fccpolycrystalline Pt phase, which may be results from structural modifications of Pt due to interaction between Pt and the second metal.⁵³ Several groups have reported that a higher catalytic performance including a higher TOF requires an optimal Pt-Pt bond distance for the electrochemical oxidation of simple alcohols and oxygen reduction reaction.^{21,38,47} In addition, Sb incorporation may cause a geometric (blocking) effect, which may promote the selective formation of the desired products on the Pt catalysts.^{22,35,38} The XRD analyses (see Fig. 2 and Table 1) indicated that the geometric structure in the bimetallic catalysts was altered by the addition of Sb or

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Bi to the Pt site, which was accompanied by an increase in lattice parameter values compared to those of pure Pt. The lattice parameters appeared to increase in the following order: Pt/C < PtSb/C < PtBi/C. In our study, a higher selectivity (68.0%) to DHA was obtained over the PtSb/C catalyst, which has a lattice parameter of 3.938 Å. The specific geometric arrangement due to the addition of Sb to Pt may affect the properties of dehydrogenative oxidation and C-C bonds breakage, leading to enhanced DHA production. For the electronic state, as shown by the changed BE and WL intensities in the XPS and XANES spectra, the electronic modification due to changing the Fermi level of the 5d Pt band states of the PtSb/C catalyst most likely affects C-H bond dissociation in the glycerol molecules as well as the adsorption/desorption properties of glycerol and other reaction products. The CV, XRD, XPS, and XANES results indicate that the bimetallic PtBi/C and PtSb/C catalysts formed alloy phases with a fcc Pt structure. PtSb/C exhibited a higher yield with a high selectivity to DHA for the electrocatalytic oxidation of glycerol. PtSb/C was highly active for the dehydrogenative oxidation of glycerol to DHA at all of the potentials in the electrocatalytic reactor system.

Reaction pathways for glycerol electrooxidation over the PtSb/C catalysts

Fig. 8 shows the possible reaction pathway over the Pt-based catalysts for glycerol electrooxidation in acidic media. The electrooxidation reaction of glycerol accompanied by breaking of the C–C, C–H, and O–H bonds can produce intermediate species on the active sites of Pt.⁵⁴ As previously shown in Fig. 6, the glycerol molecule is primarily oxidized to DHA and GAD (according to reactions (1) - (3)), which are further oxidized to GLA. Reactions (1) and (2) represent the adsorption of glycerol onto the Pt active site and the electrochemical dehydrogenative oxidation reaction, respectively. Reaction (3) represents desorption of surface DHA and/or GAD.

$$Pt + C_3 H_8 O_3 \rightarrow Pt - C_3 H_8 O_3 (ad)$$
(1)

$$Pt-C_3H_8O_3_{(ad)} \rightarrow Pt-C_3H_6O_3_{(ad)} + 2H_{(aq)} + 2e \qquad (2)$$

$$Pt-C_3H_6O_{3 (ad)} \rightarrow Pt + C_3H_6O_3$$
(3)

As the oxidation potential increased (see Fig. 6), the adsorbed DHA and GLA may be further oxidized to HPA, TTA, GCA, and OXA by cleavages of the C–C bonds.^{32,34} Based on the results in Fig. 5 and Fig. 6, the formation of DHA is favored on PtSb/C at 0.797 V, which may due to the dehydrogenative oxidation of the secondary hydroxyl groups on the glycerol molecules. These reactions are more likely to occur over PtSb/C than over other catalysts. Several groups reported that relative enrichment of Sb (see XPS analysis in Fig. 2 and Table 2) at the surface is more effective for the production of DHA than GAD due to a decrease in Pt ensemble sites for the dehydrogenative oxidation, despite the further oxidation of DHA being unavoidable, it occurred relatively slowly, which maintained the high selectivity to DHA. Therefore, the presence of Sb on the



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Fig. 8 Proposed glycerol electrooxidation sequences on Pt-based catalysts in acidic media.

surface of Pt promotes the dehydrogenative oxidation of glycerol and improves DHA selectivity.

To further explore the origins of the other products, oxidation reactions with DHA, GAD, or GLA over PtSb/C in the electrocatalytic reactor with aqueous solutions consisting of 0.5 M H₂SO₄ were also conducted under similar conditions as those used for glycerol oxidation (See Table S2 in ESI⁺). GAD was efficiently converted, and a higher GLA yield of 51.0% was achieved at 1.197 V. Interestingly, GLA was observed as a reaction intermediate from the oxidation of GAD, meanwhile GLA was not oxidized from DHA on the PtSb catalysts. These results reveal that GAD and DHA were primarily formed from the glycerol oxidation, while GLA was a secondary product from the oxidation of GAD. When DHA was used as the feedstock for the oxidation reaction, HPA, GCA, and OXA were obtained with a lower DHA conversion of 53.3% at 0.797 V. As the potential increased from 0.797 V to 1.197 V, as shown in Fig. 6(c), the DHA selectivity decreased, and the GCA selectivity gradually increased, which may indicate that DHA was an intermediate of glycerol oxidation and GCA was a byproduct from further oxidation of DHA. For the oxidation of GLA, low levels of HPA and TTA were observed, indicating that the oxidation of GLA to GCA under acidic conditions may be favored by C-C bond cleavage. This observation is consistent with the reaction mechanism discussed above. Similar evidence for two competitive pathways has been previously reported for Pt-based catalysts.^{11,20,35,38} The presence of both DHA and GAD intermediates confirms that glycerol oxidation proceeds via oxidative dehydrogenation of glycerol followed by the production of GLA from GAD accompanied by further oxidation of GLA, GCA and other intermediates over Pt-based catalysts under these conditions.

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Conclusions

In this study, we investigated the highly selective electrooxidation of glycerol to DHA by controlling the electrode potential in an electrocatalytic reactor. The selectivity of the observed products was strongly dependent on the applied potential and catalyst surface composition. Under the optimized conditions, PtSb/C served as an efficient electrocatalyst in terms of a high DHA yield of 61.4% with 90.3% glycerol conversion at 0.797 V (vs. SHE). The structural and electronic changes of the active Pt sites by adjacent Sb atoms may lead to improvement in the selectivity to the target products. Furthermore, we investigated the relationship between the applied electrode potential and the selectivity for glycerol oxidation under acidic conditions, and the results indicated that higher anode potentials promote C-C bond breaking. The electrocatalytic reactor produced a high TOF and DHA selectivity compared to a non-electrocatalytic reactor that uses an O₂ oxidant. These results may be applied to the design of a catalytic system for the efficient transformation of biomass-derived oxygenated molecules in an electrocatalytic process in the future. Along with the detailed kinetics of the reaction, a study of the selectivity of intermediate products over the catalysts in a continuous flow electrocatalytic system is currently ongoing.

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