

Electrocatalytic Oxidative Dehydrogenation of Glyoxylic Acid to Oxalic Acid and Hydrogen Gas over Palladium–Bismuth Catalyst

Mohammad Albloushi,[†] Gunnar Dunahoo,[†] Xiaopeng Liu,[†] Dev Karthikeyan Bharani, Derek Rui Zhu, Michael Galvin, Michael J. Janik,^{*} and Wenzhen Li^{*}



Cite This: <https://doi.org/10.1021/acselectrochem.6c00281>



Read Online

ACCESS |



Metrics & More



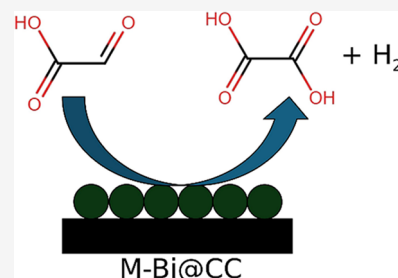
Article Recommendations



Supporting Information

ABSTRACT: Electrocatalytic oxidative dehydrogenation (EOD) of aldehydes over copper (Cu)-based catalysts enables ultralow voltage and simultaneous production of hydrogen gas (H_2) and carboxylic acids. However, Cu suffers from instability at elevated potentials, which has limited the study of the EOD process. Herein, we present palladium–bismuth bimetallic catalysts as an alternative to Cu-based catalysts for EOD. Palladium–bismuth was electrodeposited on carbon cloth using cyclic voltammetry to uniformly disperse the metals. Bipolar H_2 was produced by oxidizing glyoxylic acid at the anode via EOD and water splitting at the cathode with anodic potential between 0.625 and 1.125 V vs reversible hydrogen electrode. When approaching higher potentials, the Faradaic efficiency for the EOD reaction decreased from 77 to 12% as the electrochemical oxidation of glyoxylic acid became more favored. Density functional theory calculations suggest that the addition of Bi to Pd helps facilitate the EOD reaction by weakening CO binding, allowing for Pd–Bi to function as an oxidation catalyst at potentials where Pd electrocatalysts are CO poisoned. Despite the low Faradaic efficiency at high potentials, this study demonstrates that EOD can occur at more anodic potentials than reported for Cu-based catalysts, due to the improved oxidative stability of Bi-based catalysts.

KEYWORDS: electrocatalytic oxidative dehydrogenation, glyoxylic acid, oxalic acid, hydrogen gas, palladiumbismuth catalyst



INTRODUCTION

Hydrogen (H_2) can serve as a dense energy carrier within renewable or other less greenhouse-gas (GHG)-emitting energy processes.¹ Furthermore, H_2 is a crucial reagent in many industrial processes, including the production of ammonia as a fertilizer, the utilization of CO_2 in the reverse water–gas shift reaction, and the synthesis of hydrocarbon fuels through the Fischer–Tropsch process.² In response to rising carbon emissions from energy production via fossil fuel consumption, green H_2 production using renewable energy has attracted significant interest to address ongoing GHG emissions.³ Current methods of green H_2 production primarily rely on water electrolysis, but the costs remain high (U.S. \$3–8/kg) compared to H_2 from fossil-fuel production (U.S. \$0.5–1.7/kg).⁴ The costs associated with H_2 production through water electrolysis are limited by the high-power requirements driven by the sluggish kinetics and high thermodynamic potential of the oxygen evolution reaction (OER) at the anode.³

Traditional electrolyzers are designed to prevent gas crossover due to pressure imbalances between cathodic H_2 and anodic O_2 , thereby avoiding potentially explosive gas mixtures. The production of reactive O_2 species can also damage electrochemical cell membranes, leading to hazards and other dangerous operating conditions.^{5,6} More robust membranes, such as some ion-exchange membranes, can be used to mitigate this issue, but their use is limited due to the availability of low-cost, easy-to-

manufacture membrane materials.^{7,8} A promising alternative to address these fundamental limitations is to replace the anodic reaction with one that exhibits a lower equilibrium potential and produces higher-value chemicals than O_2 .⁹ In recent years, substantial advancements have been made in the development of paired electrolyzers for H_2 production. However, most solutions still exhibit high cell voltages with non-noble metal catalysts.^{9–11} Moreover, constrained by the mass transport of reactants in the aqueous phase, the current density is generally considerably restricted in industrial applications.^{9,12}

The electrocatalytic oxidative dehydrogenation (EOD) of aldehydes at the anode has emerged as a feasible alternative to traditional anodic OER in water electrolysis, offering lower energy requirements while simultaneously producing valuable chemicals, namely, carboxylic acids and H_2 gas as a byproduct.¹³ This approach addresses a significant constraint in green H_2 production by employing the thermodynamically favorable oxidation of organic molecules instead of water, thereby reducing

Received: June 23, 2026

Revised: August 29, 2026

Accepted: September 28, 2026

the cell voltage required for H₂ evolution and significantly improving both economic and energy efficiency.¹³ Glyoxylic acid is a promising substrate for EOD reactions because it is a simple molecule with both an aldehyde and a carboxylic acid functionality. The presence of both functional groups provides selectivity improvement. The carboxylic acid that exists in the molecule is already in its highest oxidation state, allowing the reaction to proceed on the aldehyde functional group.

Copper-based electrodes have been widely used in the electrochemical oxidation (ECO) of aldehydes to carboxylic acids. Extensive studies indicate that the surface characteristics of copper (Cu), including moderate CO* adsorption energy and effective C–H bond activation, render it an ideal candidate for facilitating the critical steps in aldehyde electrooxidation.^{14,15} A significant disadvantage of Cu is its susceptibility to surface oxidation at high anodic potentials or in elevated pH environments. This surface oxidation to Cu oxides can lead to poor catalytic activity and selectivity by shifting the EOD pathway toward ECO.¹⁴ Recent research has investigated bimetallic systems, in which the alloying of Cu with other metals enhances selectivity, stability, and Faradaic efficiency (FE) by modifying the electronic structure of the catalyst.^{16,17} Alloying strategies, especially with silver, have been employed to enhance the durability of Cu while maintaining high surface roughness and active sites during continuous use.^{2,15} Despite its apparent ultra-low-voltage requirements, durability concerns with Cu-based catalysts have led to the exploration of alternative selective catalysts for EOD reactions.

As reported by Liu et al., the mechanistic distinction between the EOD and ECO pathways can be understood at the level of individual elementary steps. Both pathways proceed through an identical initial sequence: The aldehyde (via either the carbonyl or diol route, denoted generically as R-CHO and R-CH(OH)₂, respectively) adsorbs on the metal surface, and the C–H bond is cleaved to generate an adsorbed carboxylic acid/carboxylate species, R-COOH*, together with a surface-bound hydrogen atom, H*. Notably, neither pathway bypasses this C–H cleavage step via direct hydroxyl radical addition; rather, the two mechanisms diverge only downstream of C–H activation, in the subsequent fate of the surface H* intermediate. In the EOD pathway, two adsorbed H* atoms undergo a chemical, nonelectrochemical Tafel recombination step to desorb directly as H₂ gas. Because this recombination step involves no charge transfer, the overall EOD reaction requires only a single electron transfer per aldehyde molecule consumed (RXN 1). In the ECO pathway, by contrast, the H* is instead oxidized electrochemically via a reverse-Volmer step ($H^* \rightarrow H^+ + e^-$), releasing a proton to solution and an electron to the external circuit rather than evolving H₂; this adds a second electron-transfer step, consistent with the established two-electron stoichiometry of ECO (RXN 2). This competition between the Tafel and reverse-Volmer steps is governed by a combination of thermodynamic and kinetic descriptors rather than by a distinct bond-activation mechanism. On Pt(111), for example, the C–H cleavage barrier is the lowest among the metals examined (0.39 eV), which would favor the Tafel/EOD route; however, the strong binding of CO* on Pt (−1.63 eV) necessitates a large anodic overpotential (~0.9 V_{RHE}) before appreciable oxidation current is observed, and at this elevated potential, the reverse-Volmer step becomes thermodynamically dominant, favoring ECO instead. On Cu(111), a moderate C–H cleavage barrier (0.72 eV) combined with intermediate H* binding energy (+0.31 eV) favors the Tafel step at low potentials, giving rise to the EOD pathway with an onset

as low as ~0.1 V_{RHE}. On Au(111), H* binds weakly (+0.38 eV), which would otherwise favor the Tafel/EOD route, but sluggish C–H activation (1.54 eV barrier) again necessitates large overpotentials, shifting the balance toward ECO-like behavior. Taken together, these results indicate that the EOD/ECO branching point occurs at the post-C–H-cleavage handling of the surface hydrogen intermediate (Tafel recombination vs reverse-Volmer oxidation), rather than through a separate hydroxyl-radical-mediated oxidation mechanism.¹⁴

Palladium–bismuth (PdBi) alloy catalysts, while undocumented for EOD, have shown promise in various electrochemical applications, including selective alcohol oxidation.^{18–22} This research, expanding on previous work,²³ employs electrodeposited Pd–Bi on a carbon cloth (CC) support (PdBi@CC) while using glyoxylic acid (GOA) as an aldehyde substrate. The PdBi@CC catalyst was optimized to increase selectivity for the EOD of GOA, yielding gaseous hydrogen and oxalate. This study demonstrates that pairing Bi with Pd and other noble metals eliminates the need for copper electrocatalysts while also enabling EOD to occur at higher potentials, beyond those yet to be explored for this type of reaction. Specifically, EOD was still observed at applied potentials up to 1.125 vs reversible hydrogen electrode (RHE). The improved stability of PdBi@CC enabled continuous operation for 4 h while retaining an FE near 62% for EOD at 0.825 V vs RHE.

■ MATERIALS AND METHODS

Chemicals and Materials

CT Plan Carbon cloth (Fuel Cell Store—356 μm—W0S1011), sodium(II) tetrachloropalladate (98%, Sigma-Aldrich), bismuth(III) chloride (97%, TCI America), silver nitrate (Fisher Scientific), chloroplatinic acid (Sigma-Aldrich), gold(III) chloride (Alfa Aesar), bismuth(III) nitrate (98%, Sigma-Aldrich), hydrochloric acid (Fisher Scientific), glyoxylic acid (50% solution, Sigma-Aldrich), potassium hydroxide (85%, Sigma-Aldrich), sulfuric acid (Fisher Scientific), platinum foil (0.025 mm thick, 99.9%), carbon paper (Freudenberg H23, Fuel Cell Store), Pd/C (60% palladium on Vulcan XC-72R, Fuel Cell Store), and oxalic acid (OA; Sigma-Aldrich).

Preparation of the Anodic Electrodes

CC was cut into 2.5 cm × 2.5 cm and electrochemically treated to improve its hydrophilicity.²⁴ The CC was submerged in 0.5 M sulfuric acid (H₂SO₄) as the working electrode, while using platinum (Pt) foil as the counter electrode. The CC was oxidized between 1.55 and 2.05 V vs Ag/AgCl using cyclic voltammetry (CV) over 25 cycles at a scan rate of 10 mV/s. The CC was washed with deionized (DI) water to remove any H₂SO₄ left on its surface.

To prepare the PdBi@CC, different electrodeposition solutions that each contained different ratios of Pd to Bi in their precursors were dissolved in 1.5 M HCl. For each solution, the sodium(II) tetrachloropalladate concentration was kept at 4 mM, while the bismuth(III) chloride concentration was varied to be 0.7, 2.2, 4.3, 6.5, and 8.7 mM, leading to atomic ratios in the electrodeposition solution of (2:1), (1:1), (1:2), (1:3), and (1:4), respectively. To perform the electrodeposition, a CV technique was used on the CC between −0.3 and 0.3 V (Ag/AgCl) for 5 cycles at a scan rate of 1 mV/s; this range was chosen based on the data in Table S2.

To compare PdBi@CC with Pd, 60 wt % Pd on Vulcan was applied to H23 carbon paper through spray coating. A spray ink with a concentration of 4 mg/mL was prepared using a solution comprising 88.5 vol % isopropyl alcohol, 9.8 vol % water, and 1.6 vol % of a 20 wt % Nafion solution. This catalyst ink was sonicated for 5 min before being sprayed onto a 2 × 2-cm² area of H23 carbon paper.

During spraying, the electrodes were heated to 100 °C to evaporate the isopropanol and then left on the heat plate for 10 min after spraying to ensure thorough drying.

To prepare the M-Bi@CC, where M stands for the noble metals shown in Table S2, the metal to bismuth ratio in the electrodeposition electrolyte was 1:2, which was the optimal based on the ratios tested previously. Hence, the bismuth chloride concentration was kept at 4.4 mM, while the concentration of sodium(II) tetrachloropalladate, chloroplatinic acid, and gold(III) chloride was 4, 3.8, and 2.2 mM, respectively. The potential was chosen according to the redox potentials shown in Table S2 to control the deposition amount and charge passed (40 C). The bismuth(III) nitrate and silver nitrate follow the same method with concentrations of 6.7 and 2.3 mM, respectively, except that both precursors were dissolved in 1 M nitric acid to prevent the formation of insoluble silver chloride.

Analytical Methods

Gas-phase analysis was performed using an SRI gas chromatograph (GC; Multiple Gas Analyzer #5) equipped with both a thermal conductivity detector and a flame ionization detector to quantify hydrogen gas (H₂). Liquid-phase quantification of glyoxylic acid (GOA), glycolic acid (GA), and OA was conducted using high-performance liquid chromatography (HPLC) with an Agilent Technologies 1260 Infinity II system. This system was outfitted with a variable wavelength detector and an Aminex HPX-87H column. All organic liquids were detected at 210 nm.

Even though the oxidation of glyoxylic acid can occur in two ways, ECO and EOD, the resulting liquid product from both reactions is OA according to RXN 1 and RXN 2. In addition, an aldehyde (GOA) undergoes a non-Faradaic reaction called the Cannizzaro reaction, which produces alcohol (GA) and carboxylic acid (OA) when an aldehyde is exposed to an alkaline medium. Given the simplicity of the competing reactions, the FE of EOD and ECO can be determined from a liquid product analysis. Through a system of two equations, the respective efficiencies can be determined (see eqs 1 and 2). Equation 1 represents a mole balance on the OA remaining within the post reaction liquid product. By measuring the GA produced during the reaction, the OA generated through the Cannizzaro reaction can be accounted for to determine the amount of OA created through the ECO and EOD pathways. From the amount of OA produced, an FE balance (eq 2) can be used to determine the FE for the individual reactions based on the liquid product analysis. Equation 2 assumes that ECO and EOD dominate and represent all the FE. To validate this assumption, the individual FEs determined using eqs 1 and 2 were compared to a hybrid method that also utilized GC and HPLC to quantify hydrogen gas and the liquid-phase OA to determine the EOD FE.

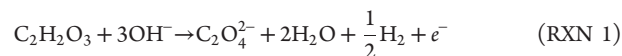
A GC was used to identify and quantify the hydrogen gas produced (mol/s). Due to the discrete frequency of GC sampling (every 2.5 min) and the likelihood of overfitting a polynomial, a Riemann sum was used to estimate the total hydrogen produced during the reaction. From the total amount of hydrogen produced over the course of the reaction, an average FE for the EOD pathway was calculated. Since hydrogen is only present in the EOD pathway, measurements of the OA concentration with HPLC facilitated the determination of the FE for ECO using a modified version of eq 2 to account for the hydrogen production. The validity of using eqs 1 and 2 to determine the FE for EOD is shown in Table S4. The discrepancies between the two methods likely stem from the inaccuracies that come from discretely measuring the hydrogen production throughout the reaction. Due to low error between the quantification methods at potentials above 0.825 V vs RHE, all results are reported using the system of equations and liquid-phase analysis to ensure the greatest consistency among all experimental conditions explored. For both methods, after each experiment, 1 mL was taken before and after the electrolysis, and immediately diluted with 19 mL of 0.1 M sulfuric acid to prevent the Cannizzaro reaction.

$$n_{\text{OA,Total}} - n_{\text{OA,Cannizzaro}} = n_{\text{OA,ECO}} + n_{\text{OA,EOD}} \quad (1)$$

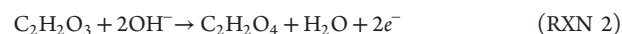
$$\frac{z_{\text{ECO}} n_{\text{OA,ECO}} F}{Q} + \frac{z_{\text{EOD}} n_{\text{OA,EOD}} F}{Q} = 100\% \quad (2)$$

where n is the number of moles, z is the number of electrons (one for EOD and two for ECO), F is Faraday constant, and Q is the total charge passed during the electrolysis.

The EOD reaction is:



The competing ECO reaction is:



Electrochemical Characterization

All electrochemical tests were performed using a Biologic VSP-300 potentiostat equipped with a ± 2 A/ ± 30 V booster. The electrolyte consisted of GOA at different concentrations in 1 M potassium hydroxide (KOH). Electrochemical half-cell measurements were conducted in a three-electrode H-cell configuration using an Ag/AgCl electrode as the reference electrode. Potentiostatic electrochemical impedance spectroscopy was conducted across a frequency spectrum of 200 kHz to 100 mHz to measure the resistance between the working and reference electrodes. The resistance value was determined as the x-axis intercept in the impedance–resistance graph.

Linear sweep voltammetry (LSV) was used to evaluate the performance of the electrodes. LSV measurements were performed at a scan rate of 5 mV/s, within a potential range of 0–1 V relative to the RHE.

Chronoamperometry (CA) was performed over a range of potentials. A potential of 0.725 V vs RHE and 30-min tests were used for comparative studies of electrode materials and electrolyte concentrations. Additional CA tests at different potentials, lasting 1 h each, were performed in a membrane-based semi-batch system to determine the catalyst's stability.

Physical Characterization

X-ray diffraction (XRD) patterns were collected on a Siemens D500 X-ray diffractometer with a Cu K α radiation source ($\lambda = 1.5406$ Å). Field-emission scanning electron microscopy (SEM) images were acquired on FEI Quanta 250. Transmission electron microscopy (TEM) imaging was acquired on a 200-kV JEOL 2100 TEM. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping were performed using a Thermo Fisher Scientific Talos F200X S/TEM operated at 200 kV and equipped with a super-X EDS system. X-ray photoelectron spectroscopy (XPS) data were collected on a Kratos Amicus XPS instrument.

Density Functional Theory Calculations

Density functional theory (DFT) calculations were performed to examine adsorption and elementary reactions on Pd(111) and Pd₂Bi₁/Pd (111) surfaces. The Vienna Ab initio Simulation Package using the Perdew, Burke, and Ernzerhof exchange–correlation functional within the generalized gradient approximation was employed for all calculations.^{25–28} An energy cutoff of 450 eV was applied to limit the plane-wave basis set. The ionic force convergence criterion was set to 0.05 eV Å^{−1} (EDIFFG), while the electronic convergence criterion was set to 10^{−5} eV (EDIFF). A Fermi smearing width of 0.2 (SIGMA) was used for surface-bound species based on the Methfessel–Paxton scheme.

The Pd(111) surface was modeled as a five-layer 3 × 3 periodic surface slab, with the top two layers relaxed to allow for surface modification and the bottom three layers frozen. The Pd₂Bi₁/Pd (111) surface model used the same lattice constants as the Pd(111) unit cell but replaced three surface Pd atoms with Bi to create a 2:1 Pd:Bi surface

ratio. The 2:1 Pd:Bi surface ratio is in reasonable agreement with the SEM-EDS results for the electrodeposited sample of the optimal composition identified. A vacuum region of 20 Å was used for all surfaces. A 4×4 by 1 k-point mesh grid was used for Pd surfaces, and a 5×5 by 1 k-point mesh grid was used for Pd–Bi surfaces.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization

SEM images reveal morphological changes in the CC substrate before and after Pd deposition. Figures S1 and S2 showed the CC substrate after Pd deposition (Pd@CC). The Pd catalyst is uniformly grown on the fiber of CC, exhibiting a cauliflower-like morphology. Further magnification reveals that the Pd species appear as closely packed nanoparticles. This hierarchical structure, composed of nanoscale Pd aggregates, is expected to substantially increase the electrochemically active surface area and provide abundant accessible active sites, while maintaining efficient electron transport through the conductive CC framework. The morphology and elemental distribution of the electrodeposited noble metal–Bi catalysts (PdBi, AuBi, AgBi, and PtBi) on CC were also characterized by SEM-EDS. As shown in Figures S3–S6, after co-deposition with Bi, the carbon fibers are uniformly covered with dense metallic deposits. At higher magnification, the deposited phases exhibit granular morphology composed of closely packed nanoparticles. The nanostructures are distributed homogeneously without apparent agglomeration, indicating uniform growth during all the electrodeposition process. Elemental mapping analysis confirmed the presence of noble metals and Bi in all samples, indicating that these elements are homogeneously distributed throughout the deposited regions, without observable phase segregation at the microscale.

The morphology of PdBi@CC catalysts with varying Pd:Bi ratios was also first observed by SEM. As shown in Figure 1, all samples exhibit a high surface coverage of electrodeposited PdBi species, indicating efficient and uniform deposition under the applied conditions. For Pd:Bi electrodeposition ratios ranging from 2:1 to 1:2, the deposited PdBi phase displays a characteristic dendritic morphology. At higher magnification, these dendritic structures are composed of nanoscale particle clusters, forming a hierarchical, plant-like architecture with abundant branch features. Furthermore, when the Bi content in the electrodeposition solution is further increased to Pd:Bi = 1:3 and 1:4, a distinct morphological transition is observed. In addition to the nanoscale-clustered features, larger aggregations and micron-scale crystalline blocks begin to appear on the fiber surface. These features suggest the formation of Bi-rich phases and indicate a deviation from the controlled dendritic growth observed at lower Bi contents. The emergence of these bulk-like or faceted particles implies that excessive Bi leads to uncontrolled growth and possible phase segregation during electrodeposition. The SEM-EDS spectra (Figure S7) further confirm the composition variation among different PdBi samples, showing relative changes in Pd and Bi signal intensities consistent with the designed deposition ratios.

XPS was employed to probe the composition-dependent evolution of the chemical states and electronic structure of Pd and Bi in the PdBi@CC catalysts with varying Pd:Bi ratios. All binding energies were calibrated with the C 1s peak at 284.8 eV. The high-resolution XPS spectrum and fitting curves of Bi 4f and Pd 3d in PdBi@CC are shown in Figure 2. The two

doublets of Bi 4f spectrum in Figure 2a can be deconvoluted to two sets of peaks for Bi (III) and Bi (0).^{29,30} Bi 4f XPS spectra reveals a distinct composition-dependent evolution in the chemical state and electronic structure of Bi within the electrodeposited PdBi catalysts. As the Pd:Bi ratio decreases from 2:1 to 1:2, the Bi (0) 4f_{7/2} peak shifts progressively to lower binding energy from 157.8 to 157.5 eV, indicative of an increasingly pronounced electronic interaction between Pd and Bi and consistent with enhanced charge transfer from Bi to Pd. The negative shift suggests that Bi is more effectively incorporated into the Pd lattice as the Bi content increases, reflecting a gradual increase in the degree of alloying. Concurrently, the relative intensity of Bi(III) increases relative to Bi(0), indicating that a greater amount of Bi is exposed at or enriched on the catalyst surface and is therefore more susceptible to surface oxidation upon air exposure. Notably, the PdBi (1:2) sample exhibits both the most negatively shifted Bi(0) feature and the highest relative Bi(III) contribution, suggesting that this composition represents an optimal state in which Pd–Bi alloying is maximized while the surface population of Bi species is also most pronounced. Upon further increasing the Bi content in the electrodeposition solution to PdBi (1:3) and PdBi (1:4), the Bi 4f peak positions exhibit only minor additional changes, indicating that the dominant Pd–Bi chemical environment is no longer substantially modified by increasing the Bi precursor concentration. This observation is consistent with the inductively coupled plasma-atomic emission spectrometry (ICP-AES) results (Table S1), for which the Bi/Pd atomic ratios of the PdBi (1:2), PdBi (1:3), and PdBi (1:4) samples remain within a relatively narrow range of 0.55, 0.51, and 0.50, respectively, despite the increasing Bi content in the electrodeposition bath. Meanwhile, SEM reveals a distinct morphological evolution at higher Bi precursor concentrations, with larger aggregates and micron-scale-faceted deposits appearing for the PdBi (1:3) and PdBi (1:4) samples. Taken together, these results suggest that further increasing the Bi precursor concentration beyond the PdBi (1:2) input composition does not lead to appreciable additional Bi incorporation into the Pd-rich alloy but instead primarily affects the morphology and growth behavior of the deposited material, potentially resulting in locally Bi-enriched or segregated regions. These results collectively indicate that PdBi (1:2) lies at the boundary between progressive alloy formation and excessive Bi accumulation. The Pd 3d XPS spectra (Figure 2b) shows two distinct peaks associated with the Pd 3d_{5/2} and 3d_{3/2}, which can be deconvoluted into three component peaks corresponding to Pd(0), PdO₂, and Pd (II).^{31,32} Compared to Bi, the Pd 3d spectra showed no pronounced composition-dependent shift, indicating that the average chemical environment and electronic state of Pd remain largely unchanged across the series. Nevertheless, the PdBi (1:2) sample exhibits the highest relative fraction of Pd(0), suggesting that metallic Pd is most effectively preserved and stabilized at this composition.

Further detailed characterization was carried out on the optimal PdBi_(1:2)@CC catalyst. As shown in Figure 3a, SEM images reveal that the catalyst forms a densely and uniformly distributed nanostructured layer on the carbon fiber surface. At higher magnification, the deposited phase exhibits a branched dendritic morphology with plant-like appearance. Further magnified TEM observations (Figure 3b,c) showed that this catalyst possesses a hierarchical architecture; even at the nanoscale, each branch is still composed of similarly branched subunits,

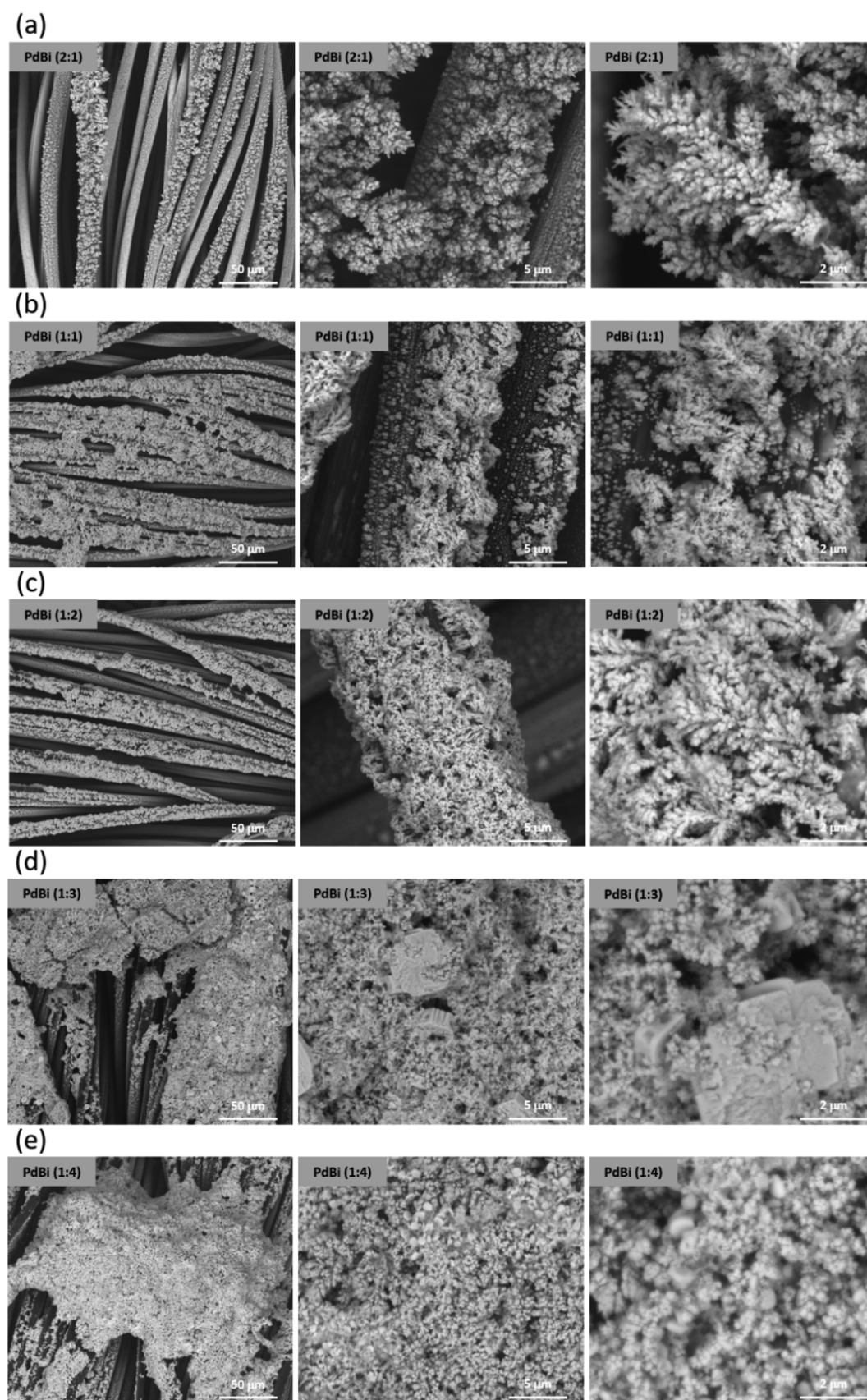


Figure 1. SEM images of PdBi@CC catalysts prepared with different Pd:Bi deposition ratios. (a) PdBi (2:1), (b) PdBi (1:1), (c) PdBi (1:2), (d) PdBi (1:3), and (e) PdBi (1:4), shown at increasing magnifications from left to right, highlighting the evolution of catalyst morphology with composition.

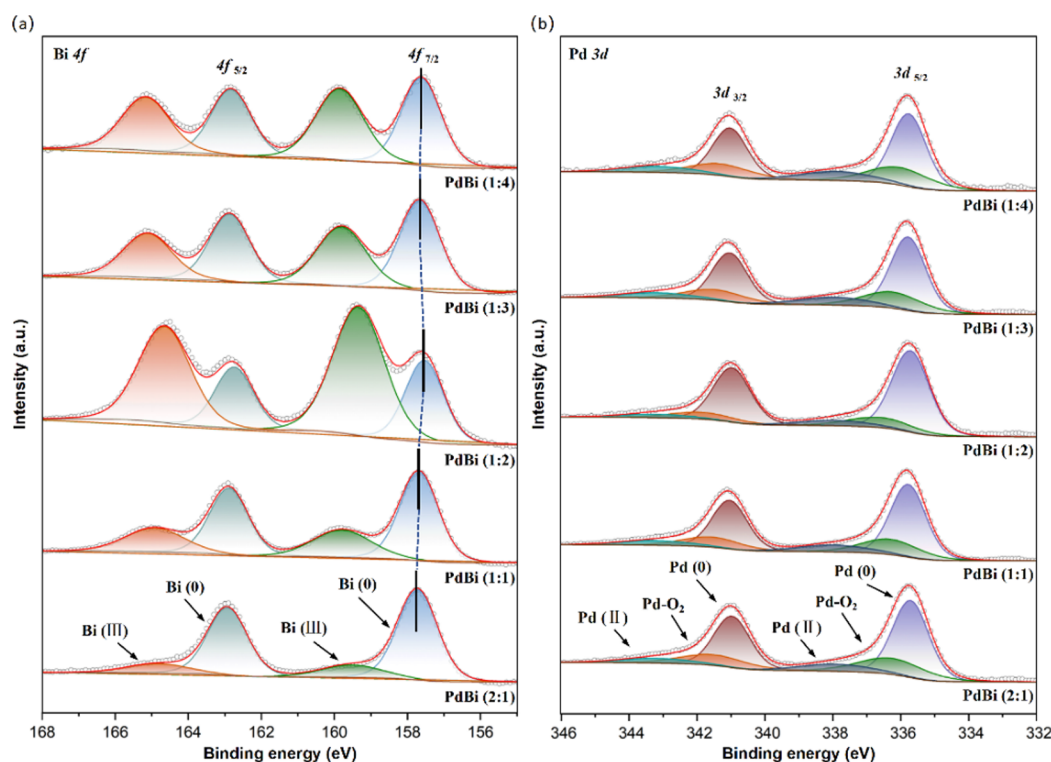


Figure 2. High-resolution XPS spectra of PdBi@CC catalysts with different Pd:Bi deposition ratios. (a) Bi 4f and (b) Pd 3d spectra of PdBi (2:1), PdBi (1:1), PdBi (1:2), PdBi (1:3), and PdBi (1:4).

indicating a multilevel self-similar growth feature. The smallest dendritic building blocks are shown in Figure 3c to consist of closely packed nanoparticles with sizes of approximately 10 nm. The TEM image in Figure 3d and Figure S8 further reveals that, within an individual particle, the lattice fringes are not aligned over a large area. Instead, the presence of lattice fringes with varying orientations within individual particles indicates the coexistence of multiple nanocrystalline crystallites separated by grain boundaries. This suggests that the dendritic structures are formed through the aggregation and coalescence of primary nanoparticles during electrodeposition rather than via single-crystal growth. This observation is consistent with the hierarchical growth mechanism in which nanosized primary particles assemble into larger structures composed of multiple crystalline domains.

The crystal structure of PdBi_(1:2)@CC was further investigated by XRD analysis. As shown in Figure 3d, diffraction peaks located at 38.5° and 43.2° can be attributed to the (111) and (200) facets of face-centered cubic Pd. Compared with pure Pd (JCPDF#46-1043), these diffraction peaks exhibit a left shift in the PdBi catalyst, indicating lattice expansion induced by the incorporation of Bi atoms into the Pd crystal lattice.³³ This lattice expansion was also confirmed by TEM (Figure 3e). Distinguishable lattice fringes were observed and measured at several different positions, the lattice spacing of 2.27–2.31 Å was slightly larger than the standard 2.24 Å of Pd (111), due to the incorporation of Bi atoms with a larger lattice spacing (2.31 Å) in Pd and the formation of PdBi alloy.^{34,35} HAADF-STEM combined with EDS was further employed to probe the elemental composition at the nanoscale. As shown in Figure 3f, Pd and Bi signals are uniformly distributed within one PdBi nanoparticle, suggesting no phase segregation and the

formation of PdBi alloy. Figure S9 showed the comparison of Bi 4f and Pd 3d of PdBi_(1:2)@CC and Pd@CC. Compared to pure Pd on CC, the binding energy of the Pd 3d_{7/2} and 3d_{5/2} peak in PdBi_(1:2)@CC shifts slightly to higher values, which indicates that the electronic structure of Pd was modified by Bi atoms doped into the Pd lattice, resulting in an electron-rich Pd state due to charge transfer from Bi to Pd.

Postreaction Structural and Compositional Characterization

To evaluate the structural and compositional evolution of the PdBi_(1:2)@CC catalyst after the 4-h stability test, a series of postreaction characterizations were conducted. SEM images show that the characteristic morphology of PdBi_(1:2)@CC is well preserved after the reaction (Figure S10), with no obvious aggregation, collapse, or large-scale surface reconstruction observed. Corresponding EDS elemental mapping further confirms that Pd and Bi remain uniformly distributed across the catalyst, indicating that the catalyst maintains its overall structural integrity and elemental homogeneity at the microscale (Figure S11). XRD analysis reveals that the main diffraction peaks of the postreaction sample shift slightly toward higher 2θ values compared with those of the fresh catalyst (Figure S12), suggesting a reduction in lattice expansion after catalysis. Meanwhile, the diffraction feature in the 30–35° region, which can be assigned to Bi₂O₃ in the fresh sample, disappears after the reaction. This result implies that part of the oxidized Bi species present before catalysis is no longer retained in the postreaction catalyst, likely due to oxidation of Bi into the solution or surface reorganization under electrochemical conditions. This interpretation is further supported by XPS results (Figure S13), in which the relative intensity of Bi(III) is

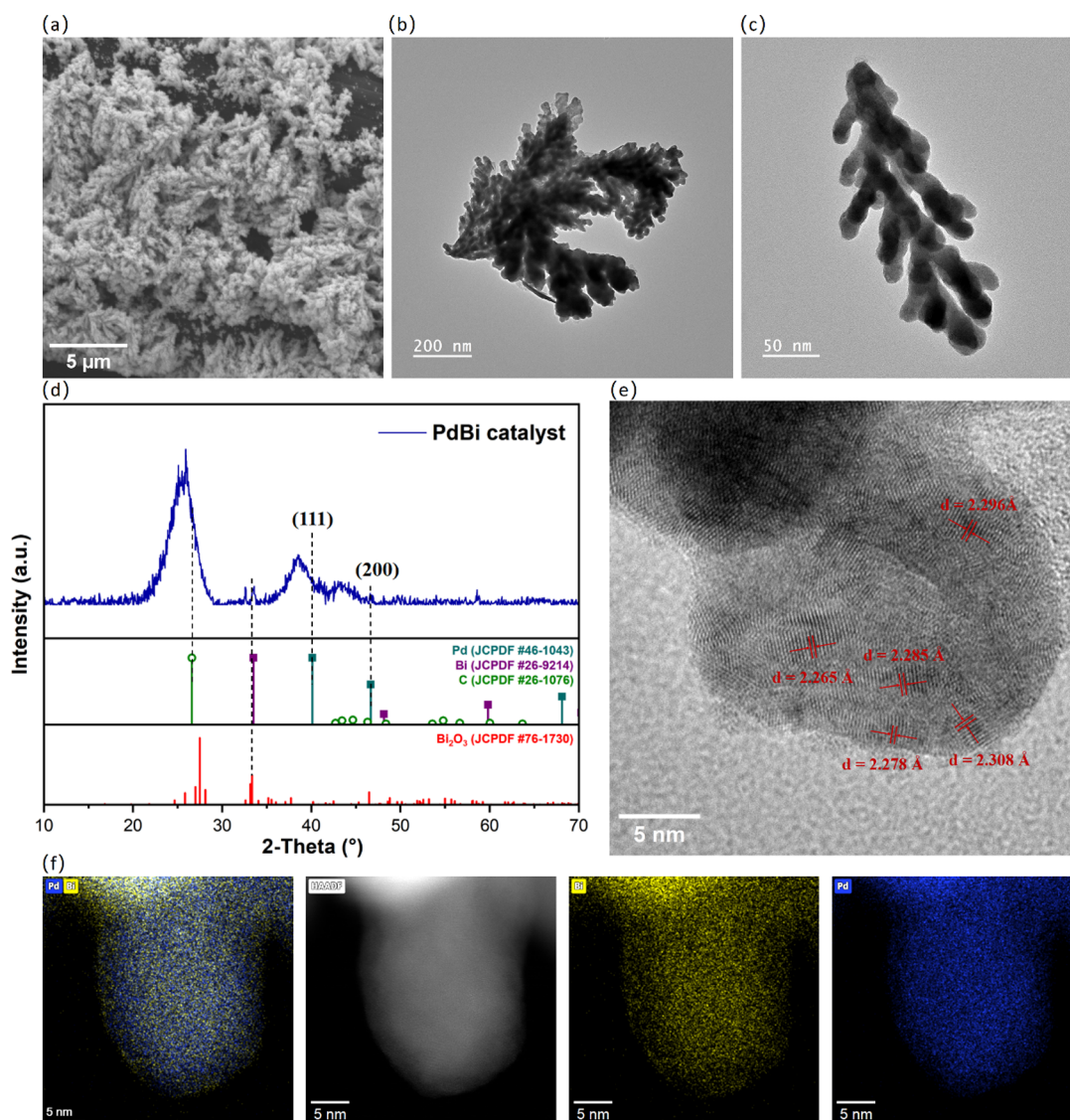


Figure 3. Structural characterization of the PdBi(1:2) catalyst. (a) SEM image, (b, c) TEM images at different magnifications, (d) XRD pattern, (e) TEM image with measured interplanar spacings, and (f) HAADF-STEM image and corresponding elemental mappings of Pd and Bi.

markedly reduced compared with that of Bi(0) after the reaction, confirming a substantial decrease in oxidized Bi species on the catalyst surface. TEM characterization further shows that the hierarchical architecture of PdBi_(1:2)@CC is well preserved at the nanoscale after catalysis, while distinct changes are observed in the local surface structure (Figure S14). In the fresh catalyst, the surface lattice fringes are generally composed of multiple small domains without large-area uniform orientation, indicating a polycrystalline and relatively disordered surface structure. However, the postreaction sample exhibits several regions with large-area, uniformly oriented lattice fringes, suggesting the emergence of more ordered surface domains after operation. The measured lattice spacings in these regions are in the range of 2.52–2.58 Å (Figure S15), which is larger than Pd-rich PdBi alloy phase, suggesting that the reaction induces the reconstruction of initially disordered and oxidized Bi-containing surface species, thereby generating a more ordered Bi-containing surface domain. Overall, the postreaction characterizations suggest that the PdBi@CC catalyst largely remains

structurally robust during the reaction, whereas its surface evolves toward a more ordered state accompanied by a substantial decrease in oxidized Bi species. Postreaction EDS mapping showed an increase in the Pd/Bi ratio from 2.22 to 3.00, confirming the loss of some oxidized Bi. This may indicate that the oxidized species were lost to the solution, as it is easier for them to be lost to the solution than to the metallic form. In addition, Table S1, ICP data, show that the used catalyst suffered a decrease in the amounts of both Pd and Bi. The decrease may look small but can significantly affect the catalyst performance, as it will be discussed in the next section.

Optimization of the Electrodeposition Method and Reaction Condition

Here, a CV technique was employed for electrodeposition. The first approach was to keep the number of cycles constant while varying the scan rate, and the second approach was to keep the scan rate constant while altering the number of cycles. Each method influences the deposition differently: The scan rate

determines how long the electrode potential stays within the deposition window per cycle. Lower scan rates allow more time at potentials where reduction occurs, resulting in greater charge transfer per cycle and higher mass loading because diffusion and growth kinetics have more time to proceed. Conversely, higher scan rates produce the opposite effect.³⁶ Number of cycles, on the other hand, adds an incremental layer of deposit, so the total deposited mass increases with the number of cycles. This means fewer cycles favor initial nucleation and produce porous interconnected structures with high surface area. In contrast, more cycles promote progressive nucleation and growth on existing nuclei, resulting in denser, more compact particles, which can sometimes block the catalyst active sites.³⁷

The electrodeposition method for this bimetallic Pd–Bi pairing was optimized to achieve the highest oxidative activity. The PdBi@CC catalyst was deposited using scan rates of 1, 2, 3, 4, 5, and 10 mV/s for 5 cycles, and the combined ECO and EOD performance was evaluated using LSV in 0.25 M GOA and 1 M KOH. An atomic Pd-to-Bi ratio of 2:1 was used for initial optimization of the CV technique. As shown in Figure 4a, the catalyst deposited at a 1-mV/s scan rate exhibited the highest current density at virtually all potentials explored. Due to its enhanced performance toward ECO and EOD, all subsequent tests were performed at a 1-mV/s scan rate.

Similar to the scan rate, PdBi@CC catalysts were deposited using a CV technique with 1–6 cycles. Due to enhanced activity at higher potentials, a cycle count of 5 was determined to produce a catalyst with the highest overall oxidative activity, as shown in Figure 4b. After the optimal deposition scan rate and cycle count were determined, the Pd:Bi atomic ratio was varied from 3:1 to 1:4 to identify the combination that yielded

the highest activity. A comparison of the catalysts (Figure 4c) shows that the ratios 2:1, 1:1, and 1:2 all yielded very similar current densities and LSV profiles. Due to their similarity, the FE for EOD was assessed using the liquid product after a 30-minute test for each catalyst.

The impact of GOA concentration on activity and EOD FE for PdBi electrodeposition solution ratios of 2:1, 1:1, 1:2, 1:3, and 1:4 was explored in an H-type cell. Table S1 shows that the ratios obtained by EDS and ICP-AES differed from those of the input during electrodeposition. This is because, during the electrodeposition of two or more metals, the one with the lower reduction overpotential will deposit faster. In Figure 5, CA tests were conducted at 0.725 V vs RHE. The PdBi@CC catalyst with an input ratio of 1:2 showed the highest FE toward EOD, with the maximum achieved at a GOA concentration of 0.5 M. To better understand how metal concentrations can affect performance, ICP analysis was conducted and summarized in Table S1. By looking at Table S1 and Figure 5, the optimal performance of PdBi_(1:2)@CC had an EOD FE nearing 80%, charge of 91 C, and Bi/Pd mass ratio of 1.07. It was also found that increasing the Bi amount in the electrodeposition solution beyond the 1:3 input ratio had no effect on the actual metal ratios in the catalyst. Specifically, this effect is shown by comparing the metal ratios of PdBi_(1:3)@CC and PdBi_(1:4)@CC, which resulted in Bi/Pd ratios of 1.0 and 0.99, respectively. Both catalysts exhibited higher charge toward EOD but lower FE than PdBi_(1:2)@CC. By ICP, all three of these catalysts showed nearly equimolar Pd:Bi ratios, even though the total metal amount deposited changed in the different electrodeposition baths. From this analysis, final Pd and Bi amounts have to be around 0.84 and 0.91 mg, respectively,

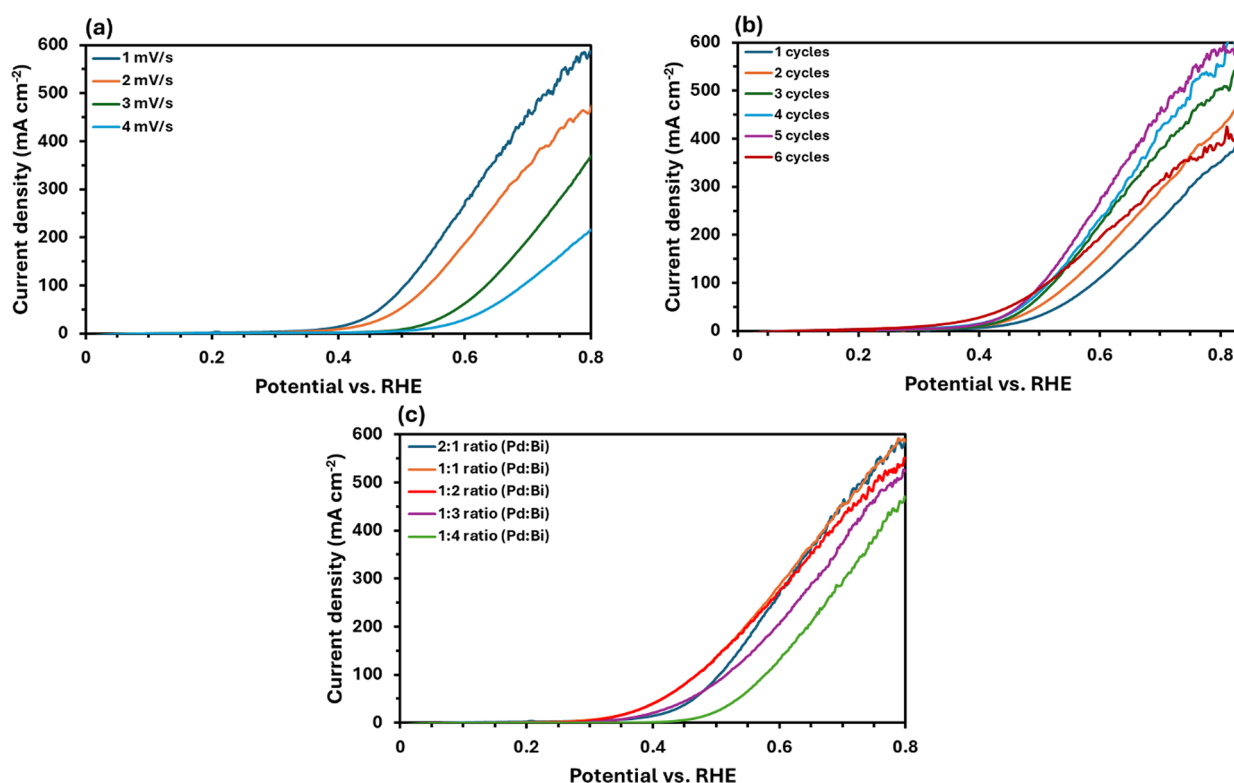


Figure 4. LSV of (a) PdBi_(2:1) prepared via different scan rates at 5 cycles, (b) PdBi_(2:1) prepared using 1 mV/s at different cycles, and (c) preparing different input atomic ratios at 5 cycles and 1 mV/s.

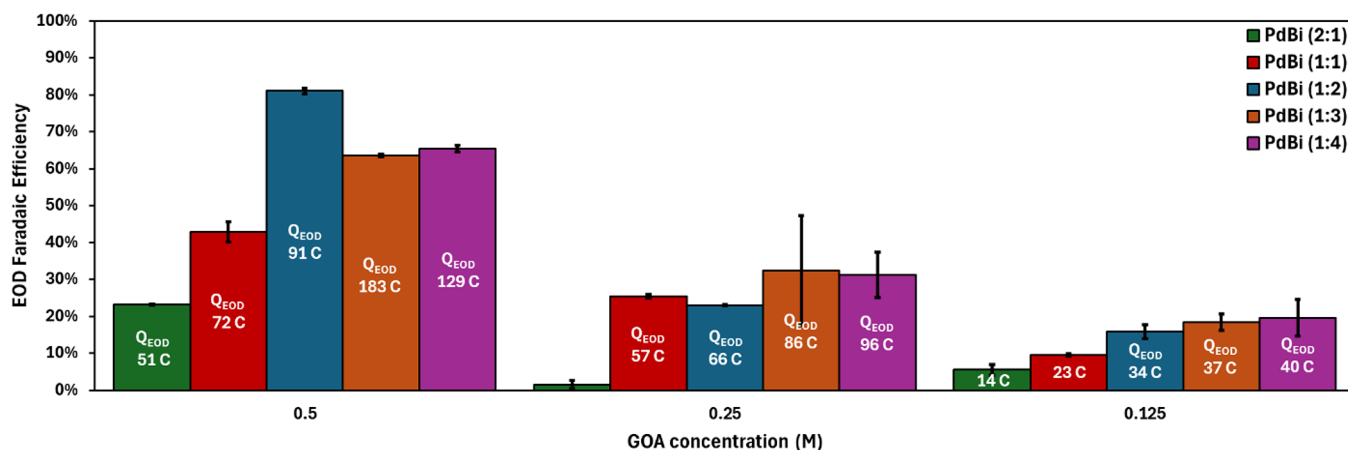


Figure 5. The different atomic ratios of Pd:Bi performance at 0.725 V vs RHE at different GOA concentrations

which were determined to be optimal for the catalyst. The remaining samples, PdBi_(2:1)@CC and PdBi_(1:1)@CC, which are Pd-rich catalysts with Bi/Pd ratios of 0.50 and 0.75, respectively, showed better performance toward ECO than toward EOD. Figure 5 also shows strong GOA concentration dependence; at 0.5 M of GOA, the catalysts were able to promote EOD while suppressing ECO. At 0.25 and 0.125 M, the FE and charge toward EOD decreased significantly across all catalysts.

Electrolysis and Assessment of Quantification Methods

Earlier, the optimal conditions to facilitate EOD of GOA were at a GOA concentration of 0.5 M in 1 M KOH and using PdBi_(1:2)@CC. To understand how the EOD reaction changes with applied potential, various CA tests were performed from 0.625 to 1.125 V vs RHE. As mentioned earlier, Cu-based electrodes would not operate at such high potentials due to the formation of Cu₂O/CuO, which starts forming at 0.6 V vs RHE or higher;¹⁴ this causes ECO to become favored. However, the shift toward ECO was not discussed, whether it was due to a change in the Cu form or the elevated potentials.

Figure 6a shows the performance of PdBi_(1:2)@CC at the mentioned potentials, where the EOD FE decreased over time as ECO began to dominate. This indicates that the EOD here is mostly potential dependent, with a cutoff of 0.825 V vs RHE, where the FE is 55% for EOD and the rest for ECO. Furthermore, as the potential increased, the charge passed did not observe any changes between 0.925 and 1.125 V vs RHE. A comparison of the cutoff potentials for the PdBi_(1:2)@CC catalyst and state-of-the-art Cu-based catalysts is shown in Table S7.

It was mentioned earlier that two methods were used to determine the EOD products and their efficiencies, using GC and HPLC. To ensure that both methods would yield the same results, the tests shown in Figure 6a were analyzed using both methods. Shown in Table S4, the highest difference between the two instruments was 5% at the lowest applied potential. This difference can be explained by the fact that HPLC quantifies the accumulated liquid product from both EOD and ECO, whereas GC quantifies only H₂. Unlike the HPLC, the GC method used samples every 2.5 min, preventing consistent measurement of the H₂ gas being produced. Furthermore, since

the tests were run at constant potential, the current density varied over time, indicating that the gas amount was not constant.

To determine whether Pd is promoting EOD or not, a commercially available Pd/C was prepared as mentioned in the Materials and Methods section, and the Pd loading was 1 mg cm⁻², as well as electrodeposited Bi on CC. Figure S17 shows that only Pd foil and 60% Pd on Vulcan (Pd/C) showed activity toward GOA, while there was less 5 mA cm⁻² on Bi@CC. In Figure 6b, Pd itself could not significantly promote EOD, but as shown in Figure 6c, the performance was more stable than PdBi_(1:2)@CC. The drop in performance for the PdBi_(1:2)@CC catalyst can be attributed to oxidized Bi leaching to the solution, which could worsen performance.

The selectivity of the EOD of furfural with PdBi_(1:2)@CC was tested to observe performance with another aldehyde. Although both contain aldehydes, the furan ring and the aldehyde location result in key structural differences. Such ECO must yield 2-furoic acid and H₂, whereas furfuryl alcohol results from the Cannizzaro reaction. Figure S16 illustrates that EOD is more favorable when GOA was used as a feedstock rather than furfural. The difference can be rooted in molecular structure and how each aldehyde interacts with PdBi surface. Specifically, GOA is much smaller than furfural and contains a α -carbonyl, which withdraws electron density, making the aldehyde carbon more electrophilic and the C–H bond existing in the aldehyde group easier to cleave.³⁸ This favors the EOD mechanism, which relies on C–H activation and dehydrogenation. GOA's compact size allows faster diffusion and less steric hindrance, leading to high turnover and the observed high charge passed.³⁹ Furfural, on the other hand, has a furan ring which enables stronger π -adsorption on Pd sites. This alters the preferred binding geometry of the aldehyde group and its hydrated intermediate, strongly favoring the classical ECO route while suppressing EOD. The aromatic system can also lead to slower desorption or mild surface passivation, which explains the lower overall current/charge passed.²

To further understand the reaction mechanism here, looking back at the same study by Liu et al., which provides a deep understanding into ECO and EOD, the reaction mechanism of GOA to OA or to OA and H₂ can be described as follows. The oxidation of glyoxylic acid to OA illustrates a fundamental mechanistic principle: the EOD and ECO pathways actually diverge well downstream of the initial C–H bond cleavage.

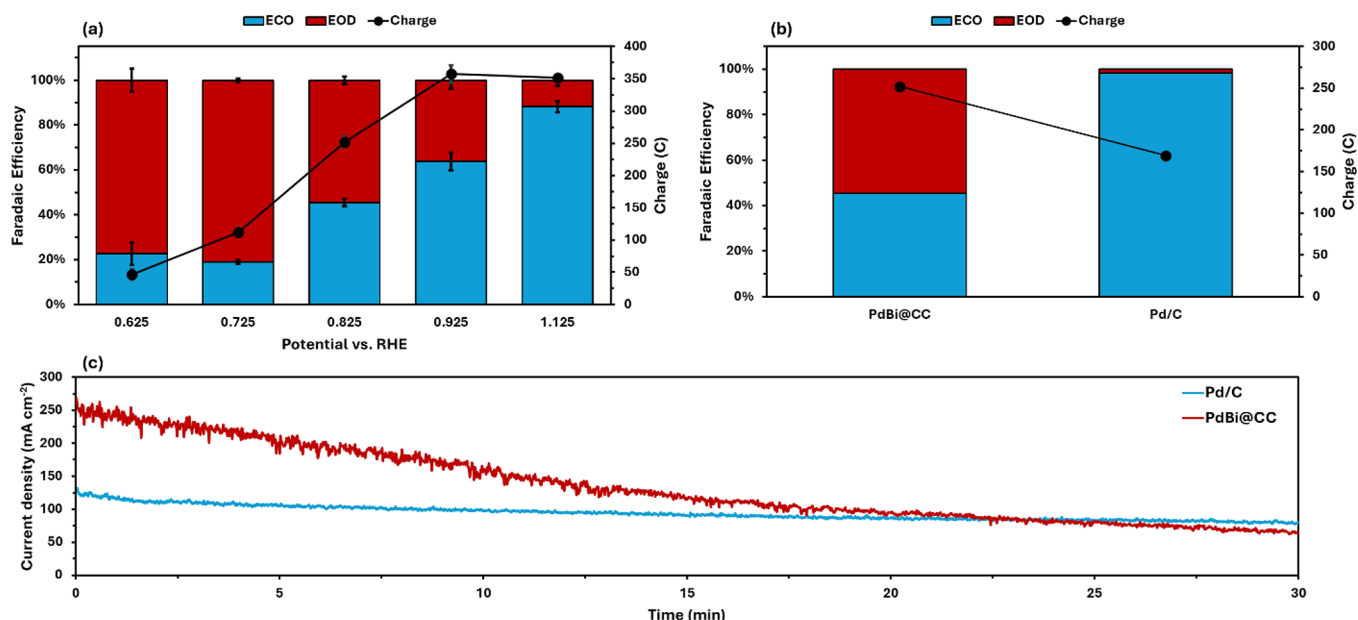


Figure 6. Chronoamperometry tests: (a) 30-min electrolysis of PdBi_(1:2)@CC at different potentials, (b) performance difference between PdBi_(1:2)@CC and Pd/C at 0.825 V vs RHE, and (c) current density profile of that shown in (b)

When glyoxylic acid adsorbs, its aldehyde group undergoes C–H scission to produce an adsorbed OA intermediate and a surface-bound hydrogen atom. What happens next with that hydrogen intermediate determines everything. In the EOD mechanism, two of these surface hydrogens simply find each other through Tafel recombination and leave as H₂ gas a purely chemical process with no electron transfer involved. This costs just one electron per glyoxylic acid molecule, and OA emerges alongside hydrogen gas as an inevitable byproduct. The ECO pathway takes a different route: instead of recombining, the surface hydrogen gets oxidized electrochemically via the reverse-Volmer step, expelling a proton and sending an electron back to the circuit. This pathway consumes two electrons per molecule but cleanly produces OA without H₂ evolution. Which pathway wins out depends on the interplay between kinetics and thermodynamics. Systems with weak hydrogen binding and facile C–H activation naturally favor the Tafel recombination route at accessible potentials. But when the system demands higher overpotentials to overcome kinetic barriers, the reverse-Volmer oxidation becomes thermodynamically competitive and often takes over. The key point is that there's no hidden third mechanism at play no separate radical pathway for direct aldehyde oxidation. The branching simply comes down to what happens to that surface hydrogen after the C–H bond breaks.

Insights from DFT Calculations

DFT calculations were used to examine the impact of Bi addition on the binding of intermediates and surface reaction energies. Figure 7 shows a representative DFT structure of the Pd₂Bi₁/Pd (111) surface described above, with the optimized orientation of GOA adsorbed in its deprotonated form on the surface.

The addition of Bi to the Pd(111) surface weakens CO adsorption, allowing oxidation at less anodic potentials than a pure Pd electrode. On pure Pd(111), hollow binding sites exhibited an adsorption energy of −2.02 eV. Aldehyde decarbonylation leads to high population of adsorbed CO on Pd

surfaces,^{40,41} with oxidation of surface bound CO then limiting oxidation electrocatalysis until high overpotentials. Pd₂–Bi₁ surface sites showed a significantly weaker CO adsorption energy of −0.87 eV. This reduced binding strength suggests that CO species are less likely to accumulate on the bimetallic surface, mitigating CO poisoning and freeing active sites for EOD turnover. As a result, the Bi addition to the Pd(111) surface suggests improved resistance to poisoning, a limited factor in using Pd or Pt catalysts for low-overpotential oxidation of aldehydes.^{42,43} CO poisoning is known to limit electrooxidation of ethylene glycol on Pd electrodes, with the additional of oxyphilic metals demonstrated to weaken CO binding to alleviate CO poisoning.⁴⁴

The alleviation of CO poisoning is likely the dominate promoting effect of Bi addition to Pd, with the Pd₂Bi/Pd(111) surface showing similar CO binding energies to the Cu(111) surface, in line with Cu electrodes also being effective for low potential aldehyde oxidation.¹⁴ A second possible mechanism through which Bi-doping promotes aldehyde oxidation is by increasing the population of adsorbed oxygen or hydroxides. Bi addition significantly strengthens OH binding to the surface (Table S5). A Higher population of adsorbed OH promotes CO oxidation kinetics, and the presence of adsorbed oxygen has been shown to significantly promote the oxidation of aldehydes as well.⁴¹

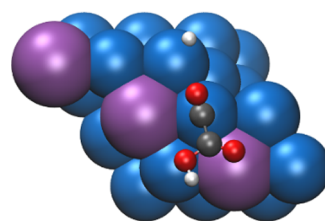


Figure 7. Optimized DFT structure of deprotonated GOA bound to the Pd₂Bi₁/Pd(111) surface slab.

A trade-off for Bi addition is that it makes the surface less effective at the GOA C–H bond dissociation step. The presence of Bi significantly decreases the binding strength of glyoxylic acid (GOA) to the surface. GOA adsorption on pure Pd was calculated to be -0.42 eV, while on the Bi-doped Pd surface, the adsorption energy approaches 0 eV, indicating nearly non-binding behavior. Direct surface-catalyzed C–H bond breaking from GOA would proceed via a nonelectrochemical dehydrogenation step, forming an adsorbed H^* . The dehydrogenation product shows negligible change in dipole moment relative to the bare surface or the adsorbed GOA state (a change of 0.02 eÅ on Pd and 0.08 eÅ on the Bi-containing surface), indicating that electron transfer is not involved in the dehydrogenation step. Prior studies have identified this C–H bond cleavage to the surface as the rate-determining step (RDS) for glycol oxidation.² The C–H dissociation step is favorable on pure Pd (-0.36 eV) but becomes unfavorable on Pd–Bi surfaces (ranging from $+0.45$ to $+1.00$ eV).

Recent studies have proposed that the active surface adsorbate may not be the aldehyde form of GOA, but rather its gem-diol, formed via the addition of water to the carbonyl in solution. To assess whether this alternative adsorbate changes the conclusions drawn above, we have computed the adsorption and C–H dissociation energetics for the gem-diol on both Pd and Pd–Bi surfaces. The same difference C–H dissociation reaction energy between the two surfaces is observed as for GOA C–H dissociation. Bi doping similarly destabilizes the surface-bound intermediate and raises the barrier for C–H bond cleavage to the metal.

H_2 production in EOD requires C–H bond dissociation, but it remains unclear if such H_2 production during EOD occurs

through a surface bound H intermediate. Experimentally, Bi doping is observed to increase EOD activity while suppressing ECO. The chemical dehydrogenation to form surface adsorbed H would presumably lead to a competition between EOD (occurring through the Tafel step combining two adsorbed H to form H_2) and ECO (occurring through a reverse-Volmer step desorbing adsorbed H as a proton). It is plausible that C–H dissociation occurs through a different pathway during EOD, in which H is transferred to a neighboring co-adsorbate rather than to the metal surface, although the involvement of the metal in facilitating C–H dissociation would need to remain, as this appears to be the main catalytic role. C–H dissociation could be facilitated by transfer to a co-adsorbate that is not disfavored and may even be promoted by the presence of Bi. This could be an O-containing species for which adsorption is promoted by Bi, as demonstrated by stronger hydroxide adsorption. We have not considered such facilitated C–H bond dissociation in this work.

Extended Electrolysis and Stability Tests

In this study, one aim was to run an extended electrolysis without interruption or the need to restart. Figure 8a shows the 1-h electrolysis of GOA, and when comparing it to the 30-min electrolysis shown in Figure 6a, the EOD did not show a significant drop in FE. However, when the electrolysis was extended to 4 h, the EOD FE decreased by almost 31%, while the ECO FE increased. This drop in FE can be attributed to the loss of Bi in the catalyst as discussed earlier. Table S6 shows the production rate and efficiencies for the first and last 2 h, calculated as separate cycles.

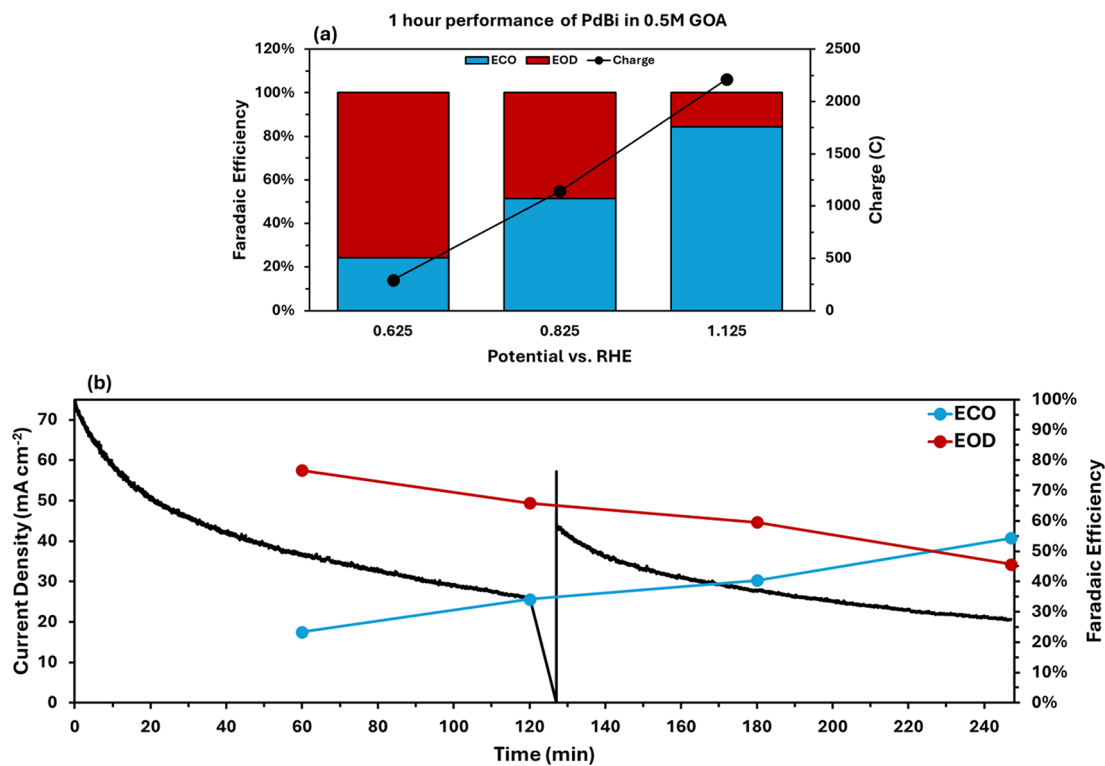


Figure 8. (a) One-hour performance of PdBi_(1:2)@CC in 0.5 M GOA at different potentials and (b) stability test at 0.825 V vs RHE using 0.5 M GOA in 1 M KOH.

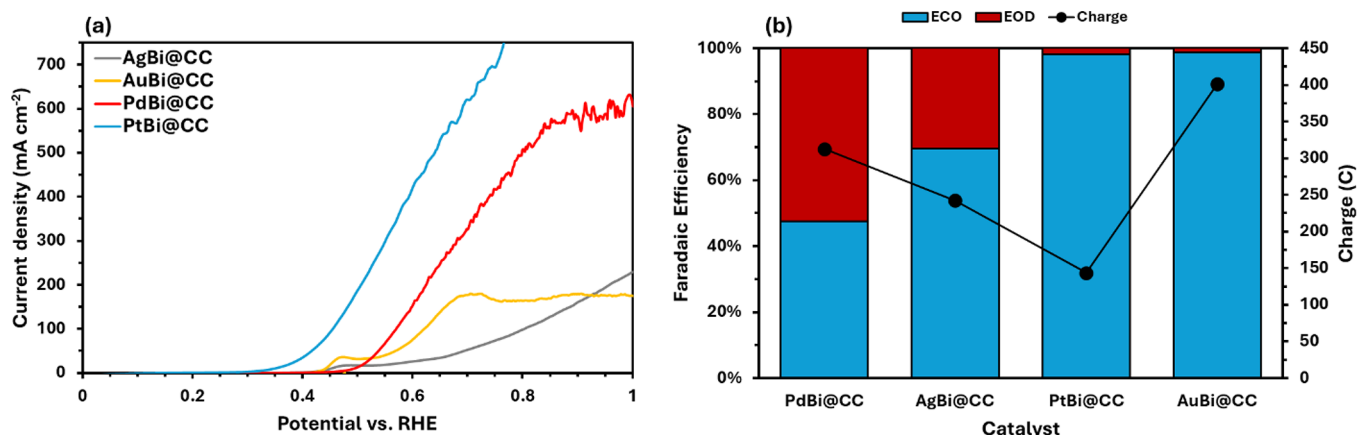


Figure 9. (a) LSV of noble metals deposited with Bi and (b) 30-min electrolysis of GOA to OA and H₂.

Evaluating Noble Metals Catalysts for the EOD Reaction

The EOD of GOA was first studied in an H-type cell with various electrodeposited noble metals along with Bi. LSV was performed with 0.5 M GOA in 1 M potassium hydroxide (KOH). As shown in Figure 9a, the following trend can be observed: Pt > Au ≈ Pd > Ag. To further assess the catalysts' selectivity toward EOD, 30 min of CA of GOA with each electrode was completed. The potential applied is based on the LSV of each metal and the system's limitations, as shown in Table S2. The PdBi@CC showed the highest selectivity toward EOD among the noble metals, as shown in Figure 8b. In a previous study, with Cu as the bimetal and the substrate, Pd was shown to have the lowest activity toward EOD compared to Pt, Au, and Ag.⁴⁵ In another study, EOD was studied at ultra-low potential, indicating that the reaction requires such a low potential to be driven.¹⁴ In Figure 9b and Table S3, Pt was run at a potential that was lowest among all of the other noble metals and showed an inferior selectivity toward EOD. Results of different noble metals shown must not be taken as final, as further improvements to the catalysts' structure, loading, morphology, and dispersion may improve the selectivity toward EOD, especially for Ag.

CONCLUSIONS

In this work, we reported an electrodeposition method for preparing a palladium–bismuth-based bimetallic catalyst for EOD to facilitate bipolar H₂ production. This work demonstrates that palladium–bismuth-based catalysts can serve as an alternative to state-of-the-art Cu-based catalysts for the EOD reaction. The current catalyst showed selectivity toward EOD between 0.625 V vs RHE and 1.125 V vs RHE, indicating that EOD can be observed beyond 0.4 V vs RHE, with an FE of 77% at 0.625 V vs RHE and 12% at 1.125 V vs RHE. The FE did not degrade when the reaction time was increased from 30 to 60 min. However, after extending the reaction time to 240 min, the process showed a drop in FE toward EOD and an increase in ECO by 31% with an average of 62% toward EOD. Further development and research on palladium–bismuth-based catalysts will deepen the understanding of how Bi facilitates the EOD reaction and the catalyst's mechanism. DFT calculations indicate that adding Bi to Pd aids the EOD reaction by reducing CO binding strength, enabling

Pd–Bi to act as an oxidation catalyst at potentials where Pd electrocatalysts become CO poisoned. This work sheds light on opportunities for further study, including different aldehyde feedstocks and scalability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acselectrochem.6c00281>.

Supplementary data covers additional catalyst characterization (physical and electrochemical), DFT results, and calibration curves (PDF)

AUTHOR INFORMATION

Corresponding Authors

Michael J. Janik – Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States; Email: mjanik@engr.psu.edu
Wenzhen Li – Department of Chemical and Biological Engineering, Iowa State University, 618 Bissell Road, Ames, Iowa 50011, United States; orcid.org/0000-0002-1020-5187; Email: wzli@iastate.edu

Authors

Mohammad Albloushi – Department of Chemical and Biological Engineering, Iowa State University, 618 Bissell Road, Ames, Iowa 50011, United States
Gunnar Dunahoo – Department of Chemical and Biological Engineering, Iowa State University, 618 Bissell Road, Ames, Iowa 50011, United States
Xiaopeng Liu – Department of Chemical and Biological Engineering, Iowa State University, 618 Bissell Road, Ames, Iowa 50011, United States
Dev Karthikeyan Bharani – Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States
Derek Rui Zhu – Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States
Michael Galvin – Department of Chemical and Biological Engineering, Iowa State University, 618 Bissell Road, Ames, Iowa 50011, United States

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acselectrochem.6c00281>

Author Contributions

[†]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by USDA (20266702145873), NSF EPSCoR (2316481), and ISU-VPR (Bioproducts Program). W.L. acknowledges his Manley Hoppe Professorship and NSF Grant (2219162, 2428214). The authors would like to thank Dr. Dapeng Jing for his help with XPS characterization and Dr. Warren Straszheim for his SEM insights. G.D. would like to thank Gary and Mickie Griswold for their philanthropic support of research through the Griswold internship program. D.K.B., D.R.Z., and M.J.J. acknowledge support from NSF Grant 2419736 and the Bridges computational resource at Pittsburgh Supercomputing Center through allocation CTS150057 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation Grants Nos. 2138259, 2138286, 2138307, 2137603, and 2138296.

REFERENCES

- Turner, J.; Sverdrup, G.; Mann, M. K.; Maness, P.-C.; Kroposki, B.; Ghirardi, M.; Evans, R. J.; Blake, D. Renewable Hydrogen Production. *Int. J. Energy Res.* **2008**, *32* (5), 379–407.
- Ramos, N. C.; Holewinski, A. Recent Advances in Anodic Hydrogen Production: Electrochemical Oxidative Dehydrogenation of Aldehydes to Carboxylates. *Curr. Opin. Electrochem.* **2024**, *45*, No. 101484.
- Luo, H.; Barrio, J.; Sunny, N.; Li, A.; Steier, L.; Shah, N.; Stephens, I. E. L.; Titirici, M. Progress and Perspectives in Photo- and Electrochemical-Oxidation of Biomass for Sustainable Chemicals and Hydrogen Production. *Adv. Energy Mater.* **2021**, *11* (43).
- International Energy Agency. *Global Hydrogen Review 2021*; Paris, **2021**.
- You, B.; Han, G.; Sun, Y. Electrocatalytic and Photocatalytic Hydrogen Evolution Integrated with Organic Oxidation. *Chem. Commun.* **2018**, *54* (47), 5943–5955.
- Feng, Q.; Yuan, X.; Liu, G.; Wei, B.; Zhang, Z.; Li, H.; Wang, H. A Review of Proton Exchange Membrane Water Electrolysis on Degradation Mechanisms and Mitigation Strategies. *J. Power Sources* **2017**, *366*, 33–55.
- Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T.; Zhuang, L. Anion-Exchange Membranes in Electrochemical Energy Systems. *Energy Environ. Sci.* **2014**, *7* (10), 3135–3191.
- Lees, E. W.; Mowbray, B. A. W.; Parlane, F. G. L.; Berlinguette, C. P. Gas Diffusion Electrodes and Membranes for CO₂ Reduction Electrolyzers. *Nat. Rev. Mater.* **2021**, *7* (1), 55–64.
- Liu, H.; Li, W. Recent Advances in Paired Electrolysis of Biomass-Derived Compounds toward Cogeneration of Value-Added Chemicals and Fuels. *Curr. Opin. Electrochem.* **2021**, *30*, No. 100795.
- Chen, G.-F.; Luo, Y.; Ding, L.-X.; Wang, H. Low-Voltage Electrolytic Hydrogen Production Derived from Efficient Water and Ethanol Oxidation on Fluorine-Modified FeOOH Anode. *ACS Catal.* **2018**, *8* (1), 526–530.
- You, B.; Liu, X.; Liu, X.; Sun, Y. Efficient H₂ Evolution Coupled with Oxidative Refining of Alcohols via A Hierarchically Porous Nickel Bifunctional Electrocatalyst. *ACS Catal.* **2017**, *7* (7), 4564–4570.
- You, B.; Liu, X.; Jiang, N.; Sun, Y. A General Strategy for Decoupled Hydrogen Production from Water Splitting by Integrating Oxidative Biomass Valorization. *J. Am. Chem. Soc.* **2016**, *138* (41), 13639–13646.
- Ramos, N. C.; Neyer, H.; Medlin, J. W.; Holewinski, A. Anodic Hydrogen Generation from Benzaldehyde on Au, Ag, and Cu: Rotating Ring-Disk Electrode Studies. *J. Electrochem. Soc.* **2024**, *171* (12), No. 126507.
- Liu, H.; Agrawal, N.; Ganguly, A.; Chen, Y.; Lee, J.; Yu, J.; Huang, W.; Mba Wright, M.; Janik, M. J.; Li, W. Ultra-Low Voltage Bipolar Hydrogen Production from Biomass-Derived Aldehydes and Water in Membrane-Less Electrolyzers. *Energy Environ. Sci.* **2022**, *15* (10), 4175–4189.
- Liu, W.; Niu, X.; Tang, J.; Liu, Q.; Luo, J.; Liu, X.; Zhou, Y. Energy-Efficient Anodic Reactions for Sustainable Hydrogen Production via Water Electrolysis. *Chem. Synt.* **2023**, *3* (4), 44..
- Feng, R.; Zhu, Q.; Chu, M.; Jia, S.; Zhai, J.; Wu, H.; Wu, P.; Han, B. Electrodeposited Cu–Pd Bimetallic Catalysts for the Selective Electroreduction of CO₂ to Ethylene. *Green Chem.* **2020**, *22* (21), 7560–7565.
- Shcherbakova-Sandu, M. P.; Gulevich, S. A.; Meshcheryakov, E. P.; Kazantseva, K. I.; Chernyavskii, A. V.; Pestryakov, A. N.; Kushwaha, A. K.; Kumar, R.; Sonwane, A. K.; Samal, S.; Kurzina, I. A. Exploring the Impact of Bi Content in Nanostructured Pd-Bi Catalysts Used for Selective Oxidation of Glucose: Synthesis, Characterization and Catalytic Properties. *Inorganics* **2025**, *13* (6), No. 205.
- Mao, Z.; Jia, L.; Mao, X.; Ding, X.; Pan, B.; Yan, T.; Xu, J.; Zhang, L.; Wang, L.; Han, N.; Li, Y. Bismuth Single-Atom Alloying of Palladium Nanosheets Promotes Selective Electrochemical Valorization of Glycerol to C₃ Products. *J. Mater. Chem. A Mater.* **2024**, *12* (36), 24136–24143.
- Zhao, P.; Qiang, L.; Xiao, H.; Ma, J.; Liu, C.; Li, X.; Zhao, M.; Jia, J. Mechanistic Insight into the Role of Bi in Bi-Rich PdBi Alloy Structure for Promoting Electrocatalytic Upcycling of Polyethylene Terephthalate Plastics into Formate. *ACS Sustainable Chem. Eng.* **2025**, *13* (24), 9279–9289.
- Lao, X.; Li, Z.; Yang, L.; Zhang, B.; Ye, W.; Fu, A.; Guo, P. Monodispersed Ultrathin Twisted PdBi Alloys Nanowires Assemblies with Tensile Strain Enhance C²⁺ Alcohols Electrooxidation. *J. Energy Chem.* **2023**, *79*, 279–290.
- Nie, Y.; Cui, Z.; Deng, L.; Li, Z.; Chen, S.; Sheng, W. Geometric-Electronic Shielding Effect: Steering the Glycerol Electrooxidation on PdBi Catalysts toward Selective Value-Added Organic Products. *J. Energy Chem.* **2026**, *112*, 814–825.
- Wang, H.; Jiao, L.; Zheng, L.; Fang, Q.; Qin, Y.; Luo, X.; Wei, X.; Hu, L.; Gu, W.; Wen, J.; Zhu, C. PdBi Single-Atom Alloy Aerogels for Efficient Ethanol Oxidation. *Adv. Funct. Mater.* **2021**, *31* (38), No. 2103465.
- Albloushi, M.; Galvin, M.; Liu, X.; Huy-Tran, N. H.; Bailey, T. A.; Dunahoo, G.; Wu, Y.; Roling, L. T.; Chen, Z.; Li, W. Unraveling the Reaction Mechanism of Ethylene Glycol Electrooxidation on Palladium–Bismuth Catalysts. *ACS Catalysis*. **2026**.
- Zhang, T.; Zhu, X.; Ye, D.-D.; Chen, R.; Zhou, Y.; Liao, Q. Cyclic Voltammetry Electrodeposition of Well-Dispersed Pd Nanoparticles on Carbon Paper as a Flow-through Anode for Microfluidic Direct Formate Fuel Cells. *Nanoscale* **2020**, *12* (39), 20270–20278.
- Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50.
- Kresse, G.; Hafner, J. *Ab Initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561.
- Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169–11186.

- (28) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (29) Dharmadhikari, V. S.; Sainkar, S. R.; Badrinarayan, S.; Goswami, A. Characterisation of Thin Films of Bismuth Oxide by X-Ray Photoelectron Spectroscopy. *J. Electron Spectros. Relat. Phenomena* **1982**, *25* (2), 181–189.
- (30) Afsin, B.; Roberts, M. W. Formation of an Oxy-Chloride Overlayer at a Bi(0001) Surface. *Spectrosc. Lett.* **1994**, *27* (1), 139–146.
- (31) Kumar, G.; Blackburn, J. R.; Albridge, R. G.; Moddeman, W. E.; Jones, M. M. Photoelectron Spectroscopy of Coordination Compounds. II. Palladium Complexes. *Inorg. Chem.* **1972**, *11* (2), 296–300.
- (32) Kim, K. S.; Gossman, A. F.; Winograd, Nicholas. X-Ray Photoelectron Spectroscopic Studies of Palladium Oxides and the Palladium-Oxygen Electrode. *Anal. Chem.* **1974**, *46* (2), 197–200.
- (33) Hong, L.; Dong, Q.; Qin, Q.; Li, H.; Xie, J.; Yu, G.; Chen, H. PdBi Alloy Nanoparticle-Enhanced Catalytic Activity toward Formic Acid Oxidation. *Int. J. Hydrogen Energy* **2019**, *44* (36), 19900–19907.
- (34) Zheng, L.; Zheng, S.; Wei, H.; Du, L.; Zhu, Z.; Chen, J.; Yang, D. Palladium/Bismuth/Copper Hierarchical Nano-Architectures for Efficient Hydrogen Evolution and Stable Hydrogen Detection. *ACS Appl. Mater. Interfaces* **2019**, *11* (6), 6248–6256.
- (35) Hu, C.; Zhai, X.; Zhao, Y.; Bian, K.; Zhang, J.; Qu, L.; Zhang, H.; Luo, H. Small-Sized PdCu Nanocapsules on 3D Graphene for High-Performance Ethanol Oxidation. *Nanoscale* **2014**, *6* (5), 2768.
- (36) Putri, N. P.; Suaebah, E.; Rohmawati, L.; Santjojo, D. J. D. H.; Masruroh, M.; Sakti, S. P. Implications of the Electrodeposition Scan Rate on the Morphology of Polyaniline Layer and the Impedance of a QCM Sensor. *Trends Sci.* **2023**, *20* (3), 6411.
- (37) Rusi, Majid, S. R. Effects of Electrodeposition Mode and Deposition Cycle on the Electrochemical Performance of MnO₂-NiO Composite Electrodes for High-Energy-Density Supercapacitors. *PLoS One* **2016**, *11* (5), No. e0154566.
- (38) Mürzt, S. D.; Zou, B.; Derichs, S.; Kümper, J.; Palkovits, R. Insights into Electro-Oxidative Dehydrogenation of Aldehydes on Copper Foam: The Role of Electrode Design, Side Reactions, and Substrate Properties. *ChemElectroChem* **2026**, *13* (1), No. e202500344.
- (39) Lucas, F. W. S.; Grim, R. G.; Tacey, S. A.; Downes, C. A.; Hasse, J.; Roman, A. M.; Farberow, C. A.; Schaidle, J. A.; Holewinski, A. Electrochemical Routes for the Valorization of Biomass-Derived Feedstocks: From Chemistry to Application. *ACS Energy Lett.* **2021**, *1205–1270*.
- (40) Williams, R. M.; Pang, S. H.; Medlin, J. W. Ring-Opening and Oxidation Pathways of Furanic Oxygenates on Oxygen-Precovered Pd(111). *J. Phys. Chem. C* **2014**, *118* (48), 27933–27943.
- (41) Mark, L. O.; Agrawal, N.; Román, A. M.; Holewinski, A.; Janik, M. J.; Medlin, J. W. Insight into the Oxidation Mechanism of Furanic Compounds on Pt(111). *ACS Catal.* **2019**, *9* (12), 11360–11370.
- (42) Román, A. M.; Hasse, J. C.; Medlin, J. W.; Holewinski, A. Elucidating Acidic Electro-Oxidation Pathways of Furfural on Platinum. *ACS Catal.* **2019**, *9* (11), 10305–10316.
- (43) Hasse, J. C.; Agrawal, N.; Janik, M. J.; Holewinski, A. ATR-SEIRAS Investigation of the Electro-Oxidation Mechanism of Biomass-Derived C₅ Furanics on Platinum Electrodes. *J. Phys. Chem. C* **2022**, *126* (16), 7054–7065.
- (44) Cheng, J.; Tu, Y.; Xiang, Y.; Ni, J.; Guo, T.; Huang, X.; Liu, B.; Wei, Z. Anti-Poisoning of CO and Carbonyl Species over Pd Catalysts during the Electrooxidation of Ethylene Glycol to Glycolic Acid at Elevated Current Density. *Chem. Sci.* **2025**, *16* (10), 4303–4310.
- (45) Liu, H.; Yu, J.; Chen, Y.; Lee, J.; Huang, W.; Li, W. Cu-Based Bimetallic Catalysts for Electrocatalytic Oxidative Dehydrogenation of Furfural with Practical Rates. *ACS Appl. Mater. Interfaces* **2023**, *15* (31), 37477–37485.