Article

Amperometric Oxygen Sensor Based on Bimetallic Pd-Cu/C Electrocatalysts

Yuan-Gee Lee ¹, Ya-Tian Hou ² and Yu-Ching Weng ^{2,*}
¹ Department of Automation Engineering, Institute of Mechatronoptic Systems, Chien-Kuo Institute of Technology, Changhua 50094, Taiwan; abj2341@gmail.com

² Department of Chemical Engineering, Feng Chia University, Taichung 40724, Taiwan; candyapplre@gmail.com

* Correspondence: ycweng@fcu.edu.tw; Tel.: +886-424517250 (ext. 3689)

Abstract: A laminated Pd-Cu alloy/C/Nafion multilayer was prepared to sense O₂ atmosphere in a metal-air structure. As a matrix, palladium was doped with various amounts of copper to conduct a preliminary test with optimum response, and four compositions, Pd, Pd₈Cu₂, Pd₆Cu₄, and Pd₅Cu₅, were selected as the candidate electrodes. It was found that the Pd₆Cu₄/C electrode showed higher sensitivity for all the electrodes. According to the phase identification of X-ray diffraction and X-ray photoelectron spectroscopy tests, the high sensitivity was attributed to the doped Cu, which was merged into the Pd matrix to repel the Pd out of the matrix as a Pd-skin layer on the surface. In the Pd-Cu alloy, the Cu site served as a template reaction site to break the O-O bond and reduce the interaction force of adsorbed oxygen on the Pd site. During the oxygen reduction reaction, not only did the decomposition of O₂ molecules occur on the electrode, but the electrode itself proceeded with a phase transformation to high valance of oxide, PdO₃. The sensing potential for O₂ sensing was determined by polarization curves in which the flat region resulting from a diffusion-control was adopted. Chronoamperometric measurements were employed to construct calibration curves for the selected electrodes. A successive response was measured to test the endurance, which showed appreciable sensitivity decay. We also tested the selectivity by introducing a series of disturbance gases, CO, SO₂, and NO₂, in which the Pd₆Cu₄ electrode prevailed over the other electrodes.

Keywords: Pd-Cu alloy/C/Nafion; multilayer; metal-air structures; template; phase transformation

Citation: Lee, Y.-G.; Hou, Y.-T.; Weng, Y.-C. Amperometric Oxygen Sensor Based on Bimetallic Pd-Cu/C Electrocatalysts. *Catalysts* **2021**, *11*, 1189. <https://doi.org/10.3390/catal11101189>

Academic Editors: Ziyaeddin Khan and Bruno Fabre

Received: 23 August 2021

Accepted: 27 September 2021

Published: 29 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Oxygen reduction reaction (ORR) plays a key role in sustainable energy conversion and green chemistry [1]. ORR is limited by slow kinetics at the cathodes. Platinum is often employed as an electrocatalyst in a cathode electrode to promote charge transfer in the ORR process. However, the high cost of Pt metal and its CO poisoning compel researchers to pay attention to substituting Pt-based cathodes [2–4]. Pd is a potential alternative to replace the Pt electrode because of its inexpensive nature and high biocompatible activity [5]. To further reduce the costs of the electrode, researchers alloyed Pd matrix with transition metal in a Pd matrix, for example, Co, Ni, and Cu. These alloyed metals do not directly reduce oxygen atoms, but play a minor role in distinguishing the reaction obstacle, and thus in promoting its electrocatalysis efficiency [6]. Cu is found to prevail over transition metals because of its widespread applications in electrocatalysis, such as nitrate [7] and oxidation of hydrazine [8]. The alloyed electrode, Pd-Cu, displayed promising performance in hydrogen purification, as it exhibited high permittivity coupled with high resistance to hydrogen embrittlement and sulfur-poisoning [9]. In the Pd-Cu alloy, Cu showed versatile characteristics that not only broke the O-O bond of the O₂ molecule, but also fast deprived the Pd electrode of absorbed oxygen atoms for further reduction to H₂O. Cu could reduce the d-band center energy of the surface Pd and weaken the interaction with the absorbed

oxygen [6]. The Cu-alloyed electrode showed higher electroactivity than the Pd electrode in ORR [10].

In this study, we prepared a metal-air electrode in which a composite structure, Pd-Cu alloy/C/Nafion, is blended as a cathode electrode to sense O₂ atmosphere. Prior to the proceeding measurement, we employed a preliminary test to sieve out the optimum Pd-Cu compositions from a series of Pd-Cu alloys. Not only was the electrochemical reaction on the electrodes explored, but also the phase transformation was found to correlate closely with the electrochemistry.

2. Results and Discussion

2.1. Microstructure Investigation of the Electrodes

Doping with Cu could collapse the lattice of the Pd matrix during oxidation. Figure 1 shows the bright field and their diffraction patterns for as-received Pd-Cu electrodes; their composition and particle size are also listed in Table 1. In Table 1, with the increased Cu amount, the particle size decreased, and thus the specific area increased till Pd5Cu5. This result is consistent with Foud-Onana's research in which the surface area of the Pd catalyst was increased by way of doping Cu to disperse Pd atoms [11]. In addition, Wu and his co-workers found a similar result that the smaller nano-particle could produce more hydrogen adsorption sites for oxygen reduction [12]. Note that the inserted diffraction pattern in Figure 1a shows a clear diffraction ring and brilliant spots. In Figure 1b–d, not only did the spots disappear, but their diffraction rings became blurry bends. This indicates that the Pd electrode initially consists of poly-well-crystallized grains. The matrix of the Pd electrode no longer maintained its lattice as blended with Cu, which results in a mismatch in bond strength between Pd-Pd and Pd-Cu. However, the binding energy of Pd-Cu bond could not continue its original Pd-Pd lattice in Figure 1a; therefore, the lattice collapses to reveal blurry diffraction bends in Figure 1b–d. We thus briefly conclude that doping with Cu could decrease the particle size and reconstruct the lattice of the Pd electrode.

Figure 1. The bright field and their diffraction patterns for different catalysts: (a) Pd/C, (b) Pd8Cu2/C, (c) Pd6Cu4/C, and (d) Pd5Cu5/C.

Table 1. Composition and particle size for different as-received Pd-Cu catalysts over carbon black support.

Catalysts	Composition (atm.%)		Particle Size (nm)
	Pd	Cu	
Pd	100	0	5.6
Pd8Cu2	85.1	14.9	4.7
Pd6Cu4	71.1	28.9	4.5
Pd5Cu5	60.0	40.0	5.4

The more the Cu merged in the electrode, the more intensively the Pd-Cu electrode oxidized. Figure 2 shows the XRD for different Pd-Cu electrodes. In the Pd pattern, a sharp peak, Pd(111) at 40.1° , and a nonsymmetrical peak, Pd(200) at 46.7° , dominate the electrode matrix. The former shows a sharp and high intensity peak to represent a well-crystallized orientation; in contrast, the latter shows a broadening and low intensity peak to imply a Pd-lattice remaining in the matrix phase. In contrast to the original Pd pattern, all the Pd-Cu alloys still retained the Pd(200) peak, which indicates a Pd phase mixing into the matrix all the way. We conclude briefly that a phase segregated over the Pd-Cu alloy, i.e., Pd-skin, which possesses a lower segregation energy, -0.2 eV/atom, than the Pd-Cu alloy [13]. The Pd(111) peak split into two peaks, Pd(111) and PdO₂(200), in a Pd8Cu2 pattern. These two peaks kept splitting into three peaks, Pd(111), PdO₂(200), and PdO₂(111), in a Pd6Cu4 pattern. Inversely, the three peaks shrink into a single peak, PdO₂(111), in a Pd5Cu5 pattern. From Pd to Pd5Cu5, the Pd electrode was oxidized to be PdO and even PdO₂ with the increased Cu amount, which illustrates the effect of doping Cu on facilitating oxidation in the Pd electrode. Note, no Cu-related peak was found in these patterns. This suggests that the doping Cu atoms were apt to incorporate the Pd matrix to show only a solid solution of Pd texture. Except for the Pd patterns, all the peaks show broadening features, which clarifies the included nano-sized grains. In contrast to the aforementioned results of the TEM diffraction patterns, the doped Cu atoms not only shrank the particles, but also were prone to collapse the Pd lattice so as to facilitate oxidation of the Pd electrode, reconfirming the previous results. In particular, the PdO₂(111) peak in the Pd5Cu5 pattern shows a broadening feature that could contain a hydrated Pd oxide in the preferred orientation (111) [14].

The Pd oxide increased the oxidation valence on the shallow layer of the electrode surface with the increase in Cu composition. Figure 3a shows the low binding energy of XPS for various compositions of Pd-Cu alloys. Note that the Pd(3d_{5/2}) peak with green color appears at 334.5 eV of the Pd spectrum; meanwhile, a PdO peak, 336 eV, with pink color appears at the same spectrum with 1.5 eV of chemical shift. As doped with Cu, the electrode was oxidized to increase the valence with a PdO₂ peak left in the Pd8Cu2 spectrum. Moreover, a PdO_x peak at 338 eV is displayed in the Pd6Cu4 spectrum with a greater chemical shift, 3.5 eV. Inversely, the chemical shift reduced with a PdO₂ peak, 337 eV, in the Pd5Cu5 spectrum. This is owing to the superficial lateral resolution, 5~20 angstrom, for XPS, which is much less than that for XRD, 1~2 μ m. The Pd-skin was apt to oxidize as PdO, PdO₂, and even PdO_x with a high chemical shift, 3.5 eV, which was identified as PdO₃ in Tura and his co-workers' research [15].

Figure 2. XRD patterns for different Pd-Cu electrodes that underwent cyclic voltammetric tests ranging from -1.0 to 0.5 V vs. Ag/AgCl.

Figure 3. Energy shift of chemical analysis of various catalysts for (a) low binding energy and (b) high binding energy.

The Cu XPS proved an oxidation-motivated effect in which Cu was merged in the lattice of the Pd matrix to facilitate oxidation. Figure 3b shows the high binding energy of XPS for Pd8Cu2, Pd6Cu4, and Pd5Cu5 in which the Cu and their oxide peaks appeared in all the spectra. In contrast, no Cu-related peak appeared in the aforementioned XRD patterns in Figure 2. This confirms the previous deduction that the Cu atom could be incorporated into the lattice of the Pd-skin to form solid solution [16]. Note that both the CuO and Cu₂O shifted to high energy with the increase in Cu composition, which emphasizes the role of Cu leading to a higher valence. Furthermore, the intensity ratio of Cu₂O to Cu in the Pd6Cu4 spectrum is less than that in the Pd8Cu2 and Pd5Cu5 spectra. This shows a lower oxidation for the Cu element in the Pd6Cu4 electrode. Compared with

the highest oxidation, PdO₃, on Pd₆Cu₄ in Figure 3a, the lower oxidation of Cu matched with the high oxidation of the Pd element. Consequently, more intensive oxidation of Pd could result in less oxidation of Cu, i.e., inactive to oxygen. We thus address an oxidation mechanism in which the Pd proceeded with an oxidation process in ORR by way of Cu oxidation first, i.e., indirect Cu oxidation [6].

2.2. Electrochemistry

Alloying with Cu in the Pd matrix changes the reaction mechanism of ORR. Figure 4 represents the cyclic voltammograms for the Pd and Pd-Cu electrodes. In the Pd voltammogram, it only shows a reduction peak, which is distinct from that with each of the two reduction peaks in the Pd₈Cu₂ and Pd₆Cu₄ voltammograms. Yeager proposed a mechanism for O₂ reduction in acid solutions in which, at low applied potential, O₂ molecules reduce with hydrogen ions [17]:

accompanied by a follow-up oxidation of hydroperoxide;

and, at high applied potential, the hydroperoxide in Equation (1) is further reduced by skipping Equation (2) in the following:

Figure 4. Cyclic voltammograms for different catalysts: (a) Pd, (b) Pd₈Cu₂, (c) Pd₆Cu₄, and (d) Pd₅Cu₅. V/s, in 0.5 M HClO₄ solution with N₂ and 1000 ppm O₂; the applied potentials were related to the Ag/AgCl reference electrode.

The voltammogram of the Pd electrode suggests a combined mechanism in which Equation (1) connected with Equation (3) in series with four charged electrons in a single high potential peak; instead, the Pd-Cu voltammograms represent two mechanisms located at low potential with Equations (1) and (2) and at high potential with Equation (3), respectively. Therefore, it was concluded the Cu changed the ORR reaction mechanism in the Pd electrode.

The applied potential for O₂ sensing was determined by the reaction mechanism in the polarization curves. Figure 5 shows the polarization curve from which we determined both the polarizing current and applied potential. For the former, the polarizing current could retain a constant diffusion layer thickness to obtain a stable response providing a dependence of response current versus O₂ concentration. For the latter, the applied potential, adopting a moderate voltage could prevent the O₂ response current from undergoing irrelative disturbance. In Figure 5, the response current for an O₂-contained solution showed a stepwise variation, including a ramp, a flat, and a steep region. In the first step, ranging from 0.4 V to −0.15 V, it contained a ramp and a flat-like region, indicating kinetic-controlled and diffusion-controlled processes. In the ramp region, the current was increased because it was related to the oxidation rate of O₂, i.e., kinetics of O₂ oxidation. The oxidation rate of O₂ was apt to reach a rush current in the high concentration of O₂; moreover, this rush current could further prolong the disturbance time, which was not a stable response. The applied potential in the ramp is excluded. In the flat region, ranging from −0.15 V to −0.25 V, the current reached a constant value regardless of the reaction rate to retain a stable current that obeyed a diffusion-controlled process. For the steep region, ranging from −0.25 V to −0.3 V, it resulted from the decomposition of water molecules, which could lead to enormous disturbance current in O₂ sensing. Therefore, the applied potential was determined at the mathematical average potential of the diffusion-controlled region, −0.20 V. Note that the response current of Pd₆Cu₄ prevails over that of all the other electrodes.

Figure 5. Polarization curves for different Pd-Cu/C electrodes when introducing 1000 ppm O₂.

Not only did the O₂ decompose on the electrode, but the energy state of the electrode was related to its reaction mechanism. The reaction mechanism is involved in bond breaking and migration of the adsorbed oxygen molecules. Prior to the electrochemical reaction, the resolved O₂ molecule had to approach an electrode by undergoing a bond-breaking process on the Cu site at the electrode/solution interface:

where $O_{ads,Cu}$ represents the adsorbed oxygen atom on the Cu site [6]. Then, the bond-broken oxygen atoms migrated to the neighbor Pd site, $O_{ads,Pd}$, as follows [16]:

where $O_{ads,Pd}$ represents the adsorbed oxygen atom on the Pd site. The $O_{ads,Pd}$ stayed on the Pd sites, undergoing the charged process with the hydrogen ion to form hydrogen peroxide as follows:

Equations (4)–(6) could be merged to amend the former reduction equation, Equation (1). Of the reduction processes from Equations (4)–(6), the critical processes are the bond-breaking of the O_2 molecule and the desorption of oxygen atom on the Pd site. The activation energy was, therefore, determined by the oxygen adsorption energy, i.e., O-O bond strength on the Cu sites, and by the energy of the oxygen atom leaving the Pd site [10]. In the Pd-Cu catalysts, Cu was in charge of breaking the O-O bond to form indirect Cu oxidation, $O_{ads,Cu}$, in Equation (4), as mentioned in the previous section. This is owing to the high activation energy of the $O_{ads,Cu}$, further reducing the oxygen atoms. The adsorbed oxygen atom in Equation (4) had to migrate to the Pd sites, $O_{ads,Pd}$, searching for low activation energy in Equation (5). The doped Cu atoms, besides breaking the O-O bond, could also weaken the O_{ads-Pd} binding in terms of the electronic interaction in which the surface Cu lowered the d-band center of the Pd surface and decreased the interaction with the oxygen adsorbate [18]. The oxygen atom on the Pd sites thus experienced charging to react with the hydrogen ion in Equation (6). Note, the lowest activation energy, 13 kJ/mol, occurred at the specific composition, Pd50Cu50 [12,19], which approaches the present optimum composition, Pd6Cu4.

The Pd6Cu4 electrode proved to be the optimum electrode with the greatest response current. A chronoamperometric measurement was employed to construct the calibration curve. Figure 6 shows the response currents for different electrodes with O_2 concentrations ranging from 100 ppm to 1000 ppm. All the curves show an instantaneous response for intermittent introduced O_2 and the stable current were adopted to construct calibration curves, as shown in Figure 7. The Pd6Cu4 electrode shows the highest sensitivity among all the electrodes, which is also consistent with that of Wang's research in which the Pd54Cu46 alloy promoted the ORR intrinsic property [20].

Appreciable sensitivity decay is found in the Pd-Cu electrodes. The sensing endurance was subject to consequent tests in which the as-received electrode was tested 20 times. Minor sensitivity decay is shown in Figure 8.

Pd-Cu electrodes show excellent selectivity. We introduced different gases that often affect the O_2 sensing, including CO, SO_2 , and NO. We found the Pd6Cu4 electrode still prevailed over the other electrodes, as shown in Figure 9.

Figure 6. Amperometric responses for various concentrations of O_2 ranging from 100 to 1000 ppm with different electrodes: (a) Pd/C, (b) Pd₈Cu₂/C, (c) Pd₆Cu₄/C, and (d) Pd₅Cu₅/C.

Figure 7. Calibration curves for different electrodes in which the applied potential was -0.2 V vs. Ag/AgCl with a gas flow rate of 300 mL/min.

Figure 8. The endurance tests for different electrodes: (a) Pd, (b) Pd8Cu2, (c) Pd6Cu4, and (d) Pd5Cu5, in which the operation condition was as follows: electrolyte 0.5 M HClO₄, applied potential -0.2 V vs. Ag/AgCl (3 M NaCl), introducing gas 100~1000 ppm O₂, and gas flow rate 300 sccm.

Figure 9. The selectivity for different electrodes, Pd/C, Pd8Cu2/C, Pd6Cu4/C, and Pd5Cu5/C, in which the operation condition was as follows: electrolyte 0.5 M HClO₄, gas flow rate 300 sccm, applied potential -0.2 V vs. Ag/AgCl (3 M NaCl), introducing gases 100~1000 ppm O₂, 100~600 ppm NO₂, 100~600 ppm SO₂, and 200~2000 ppm CO₂.

3. Materials and Methods Discussion

3.1. Glassy Carbon Substrate

A commercially available glassy carbon (GC) sheet was adopted as a catalyst support by cutting it into small slices with dimensions of 1.25 cm × 2.5 cm × 0.1 cm. These slices were immersed in an aqua regia batch for 2 h to remove the residual metal and then cleaned with de-ionic (DI) water. These just cleaned slices were cleaned in an acetone batch ultrasonically for 20 min to remove the organic coating. These slices were again cleaned with DI water and dried in a vacuum oven at 80 °C for 1 h.

3.2. Preparation for the Catalyst of Electrochemical Reaction

Reagent grade chemicals, palladium chloride (PdCl₂, Seechem Co., Seoul, Korea) and copper sulfate (CuSO₄·5H₂O, J.T. Baker Co., Phillipsburg, NJ, USA), were thoroughly dissolved in DI water and glycerin, respectively, with a molar ratio of 3:1, to form two kinds of solution with the same concentration and volume, 0.1 M and 100 mL, respectively. The former solution, PdCl₂ solution, from 100 to 0% volume ratio, was blended with the latter solution, CuSO₄ solution, from 0 to 100% volume ratio, with a concentration step of 10%, sequentially. The 11 kinds of blended solutions, Pd, PdCu₉, Pd₂Cu₈, Pd₉Cu, and Cu, were homogenized with a pulse oscillator for 10 min. Then, they were titrated and aligned on cleaned GC slices with a unit space of 1 mm. These as-titrated slices were deposited in a tube furnace (type L0185 Nabertherm Co., Lilienthal, Germany) to proceed with alloying. The slices were initially heated to 150 °C for 40 min to evaporate the solvent with a nitrogen flow, and then they were heated with a ramp 5 °C/min to 450 °C and left for 2 h.

3.3. Enhancement of the Electrocatalyst

Amounts of 0.1 M 10 mL of these determined alloyed catalysts were mixed with 0.2 g of carbon black (XC-72, 250 m²/g, Cabolt Co., Boston, MA, USA) in a solution batch with 4 M NaOH to adjust their pH value to 11 and disperse the nano-scaled catalysts homogeneously. These catalysts were then resolved in 20 mL of methanol at 70 °C for 5 h to extract the chloride ion and residual salts. The as-received catalyst solutions were filtrated and dried at 80 °C for 12 h.

3.4. Structure for O₂ Sensing

The dried catalysts were mixed with Nafion solution (5 wt%, Dupont Co., Wilmington, DE, USA) as slurries at a weight ratio of 1:8.72 in 20 mL of a DI water batch for 20 min. Nafion 117 (0.007 in, Dupont Co., Wilmington, DE, USA) sheets with a dimension of 3 cm × 3 cm were employed to serve as ion-conductive layers, which experienced a series of processes. Firstly, they were immersed in methanol for 1 h, cleaned with DI water ultrasonically, heated in 3% hydrogen peroxide solution for 1 h, and immersed in 2 M sulfuric acid solution for 1 h. Then, the prepared slurries were screen-printed with a 70-mesh screen onto the Nafion 117 sheet. The screen-printed laminates, slurry/Nafion 117, were dried in an oven at 70 °C for 3 h and then covered with air-penetrating carbon paper (GDL 10 BC, SGL group Co., Wiesbaden, Germany) as sandwich structures by hot pressing at 135 °C, 25 kg/cm² for 90 sec. The sandwich structures were trimmed to a disk shape as working electrodes with a diameter of 2.5 cm. The disk working electrode; counter electrode, i.e., Pt wire; and reference electrode, i.e., Ag/AgCl (NaCl 3 M), were equipped in a reaction tank with a volume of 3 mL and 0.5 M HClO₄ inside, as shown in the schematic plot, Figure 10. To obtain the selectivity, we introduced N₂ (99.995%, Doyang Co., Taichung, Taiwan) to dilute the tested gas, CO (200 ppm, Doyang Co., Taichung, Taiwan), SO₂ (600 ppm, Doyang Co., Taichung, Taiwan), and NO₂ (600 ppm, Doyang Co., Taichung, Taiwan).

Figure 10. Schematic plot of the air-metal sensor, in which the symbols R and C represent the reference electrode and counter electrode, respectively.

3.5. Measurements

3.5.1. Preliminary Test for the Optimum Electrochemical Reaction

To obtain the optimum composition of the alloyed catalysts, a scanning electrochemical microscope (SECM, 900C CH Instruments, Austin, TX, USA) was employed to induce a response by a tip generation-substrate collection (TG-SC) mode [21]. The resultant response current coupled with different Pd-Cu catalysts in distinct applied voltages are shown in Figure 11. Clearly, the Pd, Pd₈Cu₂, Pd₆Cu₄, and Pd₅Cu₅ electrodes showed a stronger response to the subsequent test electrodes.

Figure 11. (a) The tested spots for the Pd-Cu catalysts of different concentration ratios of PdCl₂ to CuSO₄ with a step concentration of 10%, sequentially; the images of the response intensity by TG-SC mode with SECM in ORR test with various substrate potentials: (b) 0 V, (c) -0.2 V, and (d) -0.4 V vs. Ag/AgCl purged N₂. Note that the test solution contained 0.01 M H₂SO₄ and 0.1 M Na₂SO₄; the operation conditions for the TDG-SC mode were as follows: tip to substrate distance = 50 μm , scan rate = 500 $\mu\text{m/s}$, tip current = -155 nA.

3.5.2. Investigation of the Electrode Microstructure and Electrochemistry

The morphology investigation of the catalysts and their quantitative measurement were carried out with a scanning electron microscope (SEM, S4800, Hitachi Co., Tokyo, Japan) equipped with an energy dispersive spectroscopy (EDS, EX250, Horiba Co., Kyoto, Japan). The bright field of a transmission electron microscope (TEM, 1200EX, JEOL Co., Tokyo, Japan) was employed to evaluate the particle size by ASTM E112. The phases of the catalysts were identified with an X-ray diffractometer (XRD, D8 SSS, Bruker Co., Billerica, MA, USA). The binding energy of the catalyst was measured with an X-ray photoelectron spectroscopy (XPS, PHI 500, Versa Probe Philips Co., Chanhassen, MN, USA). The electrochemical measurements were performed with a potentiostat (VersaSTAR 3, AMETEK Co., Berwyn, PA, USA).

4. Conclusions

Metal-air electrodes with a Pd-Cu alloy/C/Nafion structure were successfully prepared to sense the O₂ atmosphere in this study. The Pd-Cu alloy/C electrode showed higher sensitivity than the Pd/C electrode. The high sensitivity was attributed to the doped Cu in the Pd matrix. It was found the doped Cu atoms did not reveal the segregated Cu-related phase, but merged into the Pd lattice to form a Pd-skin layer on the surface. With the increase in dopant, Cu, the Pd-Cu electrode was apt to oxidize as PdO, PdO₂, and even PdO₃ phases. Of note, PdO₃ was found on the Pd₆Cu₄ electrode, which showed the highest sensitivity among the Pd-Cu electrodes. The specific composition of the Pd₆Cu₄ electrode confirmed the hypothesis of the optimum composition in which the Cu was responsible for breaking the O-O bond and reducing the interaction force between the adsorbed oxygen atom, O_{ads}, and Pd. For the ORR process, not only the decomposition of O₂ molecules, but also the electrode itself proceeded with a phase transformation. The specific electrode, Pd₆Cu₄, showed the highest selectivity and endurance in a series of disturbance and success tests.

Author Contributions: Conceptualization, Y.-C.W.; methodology, Y.-T.H.; formal analysis, Y.-T.H.; investigation, Y.-T.H. and Y.-G.L.; writing—original draft preparation, Y.-G.L.; writing—review and editing, Y.-C.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministry of Science and Technology, Taiwan, grant number MOST109-2221-E-035-024-MY3.

Data Availability Statement: Not applicable.

Acknowledgments: We gratefully acknowledge support from the Ministry of Science and Technology, and from Feng Chia University. The authors also appreciate the help of the Precision Instrument Support Center of Feng Chia University in providing the fabrication and measurement facilities.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Jiang, T.; Brisard, G.M. Determination of the kinetic parameters of oxygen reduction on copper using a rotating ring single crystal disk assembly (RRDCu(hkl)E). *Electrochim. Acta* **2007**, *52*, 4487–4496. [[CrossRef](#)]
2. Trens, P.; Durand, R.; Coq, B.; Coutanceau, C.; Rousseau, S.; Lamy, C. Poisoning of Pt/C catalysts by CO and its consequences over the kinetics of hydrogen chemisorption. *Appl. Catal. B* **2009**, *92*, 280–284. [[CrossRef](#)]
3. Stamenkovic, V.R.; Fowler, B.; Mun, B.S.; Wang, G.; Ross, P.N.; Lucas, C.A.; Markovic, N.M. Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. *Science* **2007**, *315*, 493–497. [[CrossRef](#)] [[PubMed](#)]
4. Koh, S.; Strasser, P. Electrocatalysis on Bimetallic Surfaces: Modifying Catalytic Reactivity for Oxygen Reduction by Voltammetric Surface Dealloying. *J. Am. Chem. Soc.* **2007**, *129*, 12624. [[CrossRef](#)]
5. Sadjadi, S.; Malmir, M.; Heravi, M.M.; Kahangi, F.G. Biocompatible starch-halloysite hybrid: An efficient support for immobilizing Pd species and developing a heterogeneous catalyst for ligand and copper free coupling reactions. *Int. J. Biol. Macromol. B* **2018**, *18*, 1903–1911. [[CrossRef](#)] [[PubMed](#)]

6. Ferná'ndez, J.L.; Walsh, D.A.; Bard, A.J. Thermodynamic Guidelines for the Design of Bimetallic Catalysts for Oxygen Electroreduction and Rapid Screening by Scanning Electrochemical Microscopy. M-Co (M: Pd, Ag, Au). *J. Am. Chem. Soc.* **2005**, *127*, 357–365. [[CrossRef](#)] [[PubMed](#)]
7. Barrabé's, N.; Just, J.; Dafinov, A.; Medina, F.; Fierro, J.L.G.; Sueiras, J.E.; Salagre, P.; Cesteros, Y. Catalytic reduction of nitrate on Pt-Cu and Pd-Cu on active carbon using continuous reactor. The effect of copper nanoparticles. *Appl. Catal. B* **2006**, *62*, 77–85. [[CrossRef](#)]
8. Kang, Q.; Wang, T.; Li, P.; Liu, L.; Chang, K.; Li, M.; Ye, J. Photocatalytic Reduction of Carbon Dioxide by Hydrous Hydrazine over Au–Cu Alloy Nanoparticles Supported on SrTiO₃/TiO₂ Coaxial Nanotube Arrays. *Angew. Chem. Int. Ed.* **2015**, *54*, 841–845. [[CrossRef](#)] [[PubMed](#)]
9. Gharibi, H.; Saadatinasab, M.; Zolfaghari, A. Hydrogen permeability and sulfur tolerance of a novel dual membrane of PdAg/PdCu layers deposited on porous stainless steel. *J. Membr. Sci.* **2013**, *447*, 355–361. [[CrossRef](#)]
10. Gobal, F.; Arab, R. A preliminary study of the electro-catalytic reduction of oxygen on Cu–Pd alloys in alkaline solution. *J. Electroanal. Chem.* **2010**, *647*, 66–73. [[CrossRef](#)]
11. Zoski, C.G. Review—Advances in Scanning Electrochemical Microscopy (SECM). *J. Electrochem. Soc.* **2016**, *163*, H3088–H3100. [[CrossRef](#)]
12. Wu, J.; Shan, S.; Luo, J.; Joseph, P.; Petkov, V.; Zhong, C.J. PdCu Nanoalloy Electrocatalysts in Oxygen Reduction Reaction: Role of Composition and Phase State in Catalytic Synergy. *Appl. Mater. Interfaces* **2015**, *7*, 25906–25913. [[CrossRef](#)] [[PubMed](#)]
13. Fouda-Onana, F.; Bah, S.; Savadogo, O. Palladium–copper alloys as catalysts for the oxygen reduction reaction in an acidic media I: Correlation between the ORR kinetic parameters and intrinsic physical properties of the alloys. *J. Electroanal. Chem.* **2009**, *636*, 1–9. [[CrossRef](#)]
14. Ruban, A.V.; Skriver, H.L.; Norskov, J.K. Surface segregation energies in transition-metal alloys. *Phys. Rev. B* **1999**, *59*, 15990. [[CrossRef](#)]
15. Peuckert, M. XPS investigation of surface oxidation layers on a platinum electrode in alkaline solution. *Electrochim. Acta* **1984**, *20*, 1315–1320. [[CrossRef](#)]
16. Tura, J.M.; Regull, P.; Victorit, L.; Castellar, M.D. XPS and IR (ATR) Analysis of Pd Oxide Films Obtained by Electrochemical Methods. *Surf. Interface Anal.* **1988**, *11*, 447–449. [[CrossRef](#)]
17. Shao, M.H.; Huang, T.; Liu, P.; Zhang, J.; Sasaki, K.; Vukmirovic, M.B.; Adzic, R.R. Palladium Monolayer and Palladium Alloy Electrocatalysts for Oxygen Reduction. *Langmuir* **2006**, *22*, 10409–10415. [[CrossRef](#)]
18. Yeager, E. Electrocatalysts for O₂ reduction. *Electrochim. Acta* **1984**, *29*, 1527–1537. [[CrossRef](#)]
19. Tang, W.; Zhang, L.; Henkelman, G. Catalytic Activity of Pd/Cu Random Alloy Nanoparticles for Oxygen Reduction. *J. Phys. Chem. Lett.* **2011**, *2*, 1328–1331. [[CrossRef](#)]
20. Wang, X.; Kariuki, N.; Vaughey, J.T.; Goodpaster, J.; Kumar, R.; Myers, D.J. Bimetallic Pd–Cu Oxygen Reduction Electrocatalysts. *J. Electrochem. Soc.* **2008**, *155*, B602–B609. [[CrossRef](#)]
21. Ye, H.; Crooks, R.M. Effect of Elemental Composition of PtPd Bimetallic Nanoparticles Containing an Average of 180 Atoms on the Kinetics of the Electrochemical Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2007**, *129*, 3627–3633. [[CrossRef](#)] [[PubMed](#)]