

Article

Preparation of Nanoporous PdIrZn Alloy Catalyst by Dissolving Excess ZnO for Cathode of High-Temperature Polymer Electrolyte Membrane Fuel Cells

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Abstract: Carbon-supported nanoporous palladium-iridium–zinc (NP-PdIrZn) electrocatalyst was prepared through the modification of the alcohol-reduction process following the selective dissolution of excess ZnO nanoparticles using NaOH solution. The electrocatalyst was applied successfully to the cathode for a high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC). X-ray diffraction (XRD) patterns of the NP-PdIrZn nanoparticles suggests formation of the ternary alloy and complete removal of ZnO without the formation of individual Pd, Ir, or Zn nanoparticles. Moreover, transmission electron microscopy (TEM) images displayed porous nanoparticles with an irregular shape, which was generated by removing the ZnO from the PdIrZn–ZnO nanocomposites, and was prepared by using the excessive Zn precursor. The electrochemical surface area (ECSA) of the NP-PdIrZn catalysts was estimated by cyclic voltammetry using a rotating disk electrode method, and the oxygen reduction reaction (ORR) activity was evaluated by a linear sweep method. The NP-PdIrZn catalysts showed larger ECSA and higher ORR activity than those of the PdIr and PdIrZn catalysts, which may be attributed to the increased exposed surface area by selective etching of the ZnO in the composites. Furthermore, the NP-PdIrZn catalyst exhibited excellent performance (0.66 V) in a single cell under the HT-PEMFC condition than those of the PdIr (0.58 V) and PdIrZn (0.62 V) catalysts, indicating that geometric and electronic control of Pd-based alloy can improve the single-cell performance for the HT-PEMFC.

Keywords: PdIrZn alloys; nanoporous structure; oxygen reduction reaction; cathode; high-temperature polymer electrolyte membrane fuel cell

1. Introduction

For a recent decade, polymer electrolyte membrane fuel cells (PEMFCs) have received attention for their application as an energy conversion solution in the transportation, auxiliary power, and combined heat and power (CHP) areas [1–4]. Among them, CHP devices using high-temperature PEMFC (HT-PEMFC), which can generate heat and electricity concurrently, are adopted to decrease the generation of carbon dioxide. HT-PEMFC, which is a kind of PEMFC operating in the range of 120–200 °C, used the phosphoric acid (PA)-doped polymer membranes [5–7] as a proton conductor. Thus, it does not need humidification and provides high tolerance to CO or other impurities [8]. In addition, the activity electrocatalyst toward the oxygen reduction reaction (ORR) in the HT-PEMFC

may increase due to the operation temperature [9,10]. These features allow for compact systems through the removal of the large humidifier and partial oxidation part in the reformer. However, the power density from HT-PEMFC showed a lower value than that of low-temperature PEMFC (LT-PEMFC), which is operated below 100 °C, because of the large loss in the activation region by PA poisoning on the Pt catalyst [9,10]. Thus, a large amount of Pt is demanded in the electrode to secure sufficient power density and long durability, which is a significant issue for HT-PEMFC. Numerous researchers have been investigating highly active non-Pt catalysts to replace Pt catalysts and reduce the cost of fuel cells [11–21]. Among precious metals, the Pd has a similar valence electronic configuration. However, Pd-based catalysts typically display lower activity and stability toward ORR than those of Pt catalysts [16].

One strategy for increasing the ORR activity of Pd-based catalysts to a similar level to Pt is the alloying of Pd with transition metals, such as Cu, Co, Ni, and Fe to alter the electronic structure of Pd [14–22]. Walsh et al. synthesized carbon-supported PdV bimetallic catalysts with a nominal V amount in the range of 20% to 40% and reported enhanced electrocatalytic activity and durability for ORR. A PdV/C catalyst with Pd:V (7:3) and heat-treated at 300 °C was described as a promising catalyst for ORR, suggesting that changes in the interatomic distance and surface electronic structure of Pd atoms, due to alloying with V, play a key role in enhancing the ORR activity [23]. Bebelis et al. studied PdZn/C bimetallic electrocatalysts prepared by wet impregnation and a gas reduction process. They found that a catalyst with a 3:1 Pd:Zn mass ratio resulted in an enhanced specific activity for ORR compared to those of Pd/C catalysts and other PdZn/C catalysts [24]. Shul et al. reported a trimetallic catalyst with Pd, Fe, and Mo with an optimized Pd:Fe:Mo atomic ratio of 7.5:1.5:1.0 and heat-treated at 500 °C. This catalyst displayed both high catalytic activity and stability towards ORR; Mo in the catalyst acted as a stabilizer that interrupted the dissolution of Fe and Pd [25].

In general, the modification of the 4d orbital in a Pd atom, by alloying it with transition metals, is known to enhance the ORR activity due to the contraction of the Pd–Pd spacing in the alloy nanoparticles and the decrease in the Pd–O bond strength [26]. However, the inherently weak durability correlated with the low redox potentials of Pd and transition metals limits their applications. Contrary to Pd and other metals, Ir has a higher redox potential of 1.16 V, which is stable in acidic media. It is well known that Ir can improve the durability of Pd-based alloy catalysts [27–33]. Yang et al. demonstrated that PdIr catalysts with a nanowire or nanodendritic structure display high activity and durability for ORR, which may be mostly due to the modified electron structure of Pd and the protective effect of Ir [28]. Although Ir has been effectively adopted to increase the catalytic activity and durability of Pd alloy catalysts for ORR, it still does not reach the activity of Pt. Recently, several studies on PdIr-based trimetallic catalysts alloyed with transition metals, such as Y, Co, and Ni have been conducted, showing that these catalysts improve the ORR activity [29–33].

Another strategy to extend the ORR activity of Pd alloys is the modification of the morphology of the nanoparticles. Nanoporous materials fabricated using a dealloying method or selective etching have received attention as the distinctive combination of a highly conductive network and a number of accessible, open nanopores in the structure are advantageous for electron and mass transport during the electrocatalytic reactions [34–37]. Yang et al. suggested that de-alloyed PdCu electrocatalysts have superior activities for ORR than that of pure Pd [34]. Zhang et al. reported that nanoporous PdCu alloys with uniform size and adjustable bimetallic ratios, prepared by etching Al from the ternary PdCuAl alloy in a sulfuric acid solution, result in significantly improved electrocatalytic activity and structural stability in ORR contrasted to those of commercial Pt/C catalysts [35]. In addition, they also studied nanoporous PdZr and PdCr alloys that show not only higher specific and mass activity but also better durability towards ORR [36,37]. Consequently, Pd-based alloy catalysts with a nanoporous structure may be significantly promising cathode catalysts with superior ORR activity.

The objective of this work is to resolve the above-mentioned challenges by investigating a novel nanoporous alloy catalyst consisting of Pd, Ir, and Zn atoms that can increase the ORR activity in the cathode of HT-PEMFC. By dissolving the ZnO nanoparticles from the ternary alloy nanoparticles,

nanoporous PdIrZn (NP-PdIrZn) alloy nanoparticles were obtained, resulting in the enlargement of the electrochemical surface area (ECSA) and consequently improving the ORR activity. Figure 1 shows a schematic of the nanoporous PdIrZn catalyst for a better understanding of the catalytic nanoparticle structure.

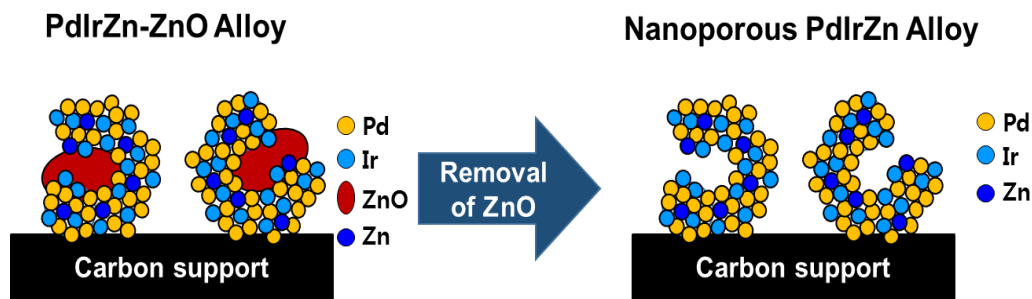


Figure 1. Schematic for the preparation of the nanoporous (NP)-PdIrZn catalyst.

2. Materials and Methods

2.1. Preparation of Nanoporous PdIrZn Catalysts

The NP-PdIrZn catalyst was prepared by a modification of the alcohol reduction method. At first, 0.1 g of carbon (Ketjen Black 300 J, surface area = 800 m²/g) was dispersed in 48 g of a water and isopropyl alcohol (IPA) solution (the water: IPA weight ratio was 67:33). An aqueous solution of 0.108 g of K₂PdCl₄·H₂O (Umicore), 0.137 g of H₂IrCl₆·6H₂O (Umicore), 0.138 g of Zn(NO₃)₂·6H₂O, and 0.256 g of sodium citrate in 30 g of water was combined to the carbon-dispersed solution. The pH of the stirred mixture was controlled to ~11 using 1 M NaOH aqueous solution. The resultant mixture was thermally treated in a microwave reactor at 160 °C for 1 h. The mixture was then centrifuged and the solid contents were washed with deionized water 4 times. The solid powders were then dried in a freeze dryer to obtain 50 wt.% PdIrZn–ZnO composites on a carbon support. The catalyst was then ramped up to 300 °C at an increasing rate of 50 °C/h and retained at this temperature for 2 h under an H₂ flow, followed by treatment with 1 M NaOH solution at room temperature (RT) for 1 h to remove the nano-sized ZnO. For comparison, the PdIr catalyst was prepared using the same amount of Pd and Ir precursors. PdIrZn catalysts supported on carbon were prepared by a one-step alcohol reduction process using the same amount of Pd and Ir compounds and reduced amount (one third for NP-PdIrZn) of Zn precursors to avoid the formation of ZnO.

2.2. Physicochemical and Electrochemical Characterization of Catalysts

X-ray diffraction (XRD) patterns were measured using a Philips X'pert Pro X-ray diffractometer using a Cu-K α source at 40 kV and 40 mA. The crystalline sizes of the Pd alloy on the carbon support were calculated by using the Scherrer's equation [38]. A G2 FE-TEM Tecnai microscope was used to obtain transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and high-angle annular dark-field (HAADF) images at an accelerating voltage of 200 kV. The loading of metal elements in the Pd alloy catalysts was estimated using inductively-coupled plasma atomic emission spectroscopy (ICP-AES) with a 40.68 MHz RF source (Jobin Yvon 2301).

The electrochemical properties of the catalysts were determined by creating an electrochemical cell using a counter electrode, a reference electrode, and a rotating disk electrode as a working electrode. For determining the ECSA, the cyclic voltammogram (CV) was measured in the range of 0.05–1.2 V (versus normal hydrogen electrode [NHE]) at RT in 0.1 M HClO₄ solution, which was saturated with N₂ by bubbling the gas through the solution for 30 min using 60 μ g/cm² of catalyst with a scan rate of 20 mV/s [39]. The ECSA of the Pd alloy in the catalyst was calculated from the integrated area of the hydrogen desorption region in the CV with the potential range of 0.05–0.4 V, as the previous literature [39,40]. A linear scan voltammogram of the ORR was scanned at a scan rate of 5 mV/s in 0.1

M HClO₄ solution at RT, which was saturated with pure O₂ by bubbling the gas through the solution for 30 min.

2.3. Measurement of Membrane Electrode Assembly Performance

The cathode consisted of Pd alloys supported on carbon and polyvinylidene fluoride (PVDF, Aldrich). The anode consisted of commercial PtRu alloys supported on carbon (Tanaka Kikinzoku Kogyo (TKK)) and PVDF. The catalyst slurry was mixed using a PVDF solution and *n*-methyl-2-pyrrolidone (NMP). The amount of NMP was changed by the catalysts. For comparison, the cathode using a commercial 50 wt.% PtCo (TKK) was prepared by the same procedure. The catalyst slurry was coated onto a gas diffusion substrate (35BC) purchased from SGL utilizing a custom-made bar coater. The amount of doped PA in the polymer membrane for HT-PEMFCs was regulated at 300% by dipping a dry membrane in 85 wt.% PA. Dry H₂ gas (flow rate: 100 cm³/min) and dry air (flow rate: 250 cm³/min) was used for the anode and cathode, respectively. The membrane electrode assembly (MEA) was operated in the galvanostatic mode at 0.2 A/cm and 150 °C to record the voltage. The actual sizes of the electrode in the MEA were 2.8 cm × 2.8 cm. Details regarding the assembly and the operation of the MEA are available elsewhere [41,42].

3. Results and Discussion

3.1. Physicochemical Characterization of Pd Alloy Catalysts

Nanoporous materials are important scientifically and technologically in heterogeneous catalysis because they deliver a high surface area per unit mass of the catalyst and suggest the increased possibility of interactions between the active components and reactants [43]. Therefore, they are promising for use in catalytic applications. Chemical dealloying or selective etching, which involves the selective removal of the non-noble metal component from an alloy, results in a porous structure with nano-sized pores [44]. We prepared carbon-supported nanoporous ternary PdIrZn alloy by chemically etching nano-sized ZnO in PdIrZn–ZnO nanocomposites. The microstructures of the Pd alloy catalysts were investigated by TEM observations (Figure 2). It was detected that all of the PdIr alloy nanoparticles are uniformly distributed on the carbon support. The average particle sizes of the PdIr, PdIrZn, and NP-PdIrZn catalysts, obtained by the analysis of more than 100 nanoparticles in the corresponding TEM images, are 7.7 nm, 7.8 nm, and 7.3 nm, respectively, which imply that the modified alcohol method can provide the nanoparticles of ~8 nm regardless of the alloy composition. A clear difference in the morphology of the alloy nanoparticles is observed in the insets of Figure 2. The TEM image (inset of Figure 2c) of the NP-PdIrZn nanoparticles shows the open-pore surrounded by the agglomeration of small nanoparticles or grains of PdIrZn, which is generated by the dissolution of ZnO using chemical etching in the NaOH solution. It is supported by the change in the XRD patterns, as shown in Figure 3. On the contrary, the dense PdIr and PdIrZn nanoparticles are observed in the inset of Figure 2a,b, respectively. This observation is supported by the previous reports, which suggested that selective dissolution or etching of non-active elements from metal alloys results in a nanoporous alloy structure [35–37,45]. In addition, EDX analysis verified the presence of Pd, Ir, and Zn in the NP-PdIrZn particles as displayed in Figure 2d.

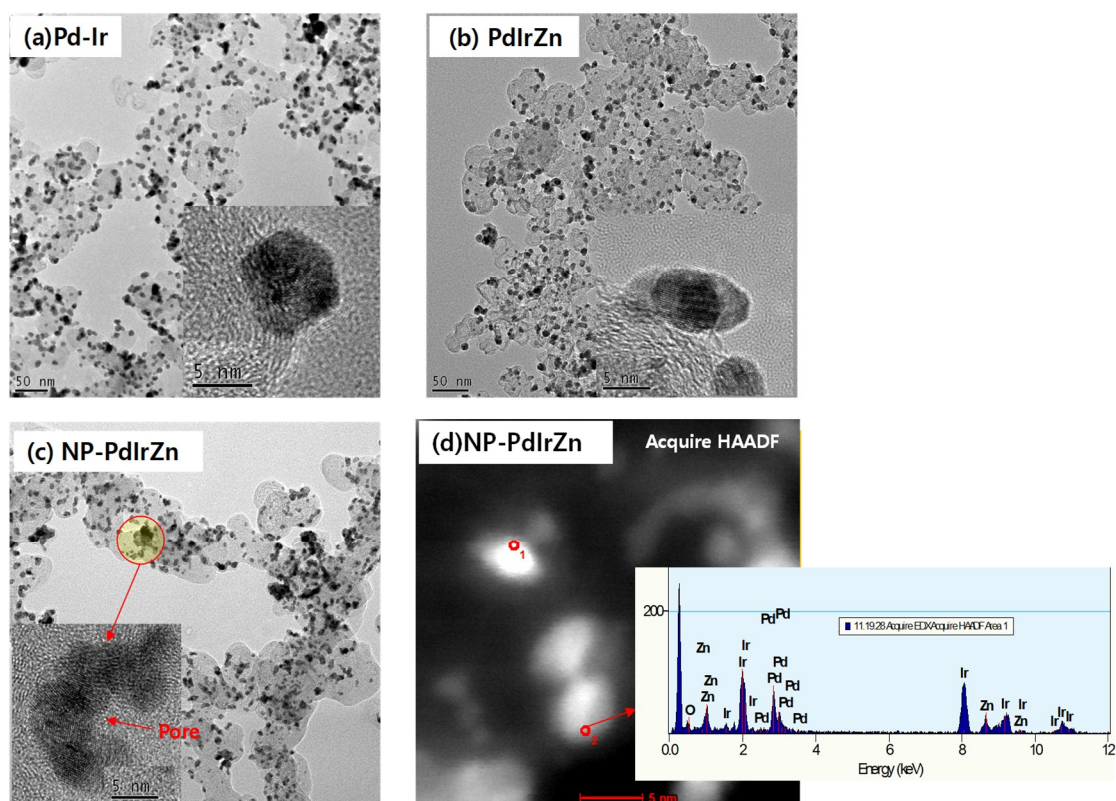


Figure 2. TEM images of (a) PdIr, (b) PdIrZn, and (c) NP-PdIrZn catalysts, and (d) TEM-EDX image of the NP-PdIrZn catalyst.

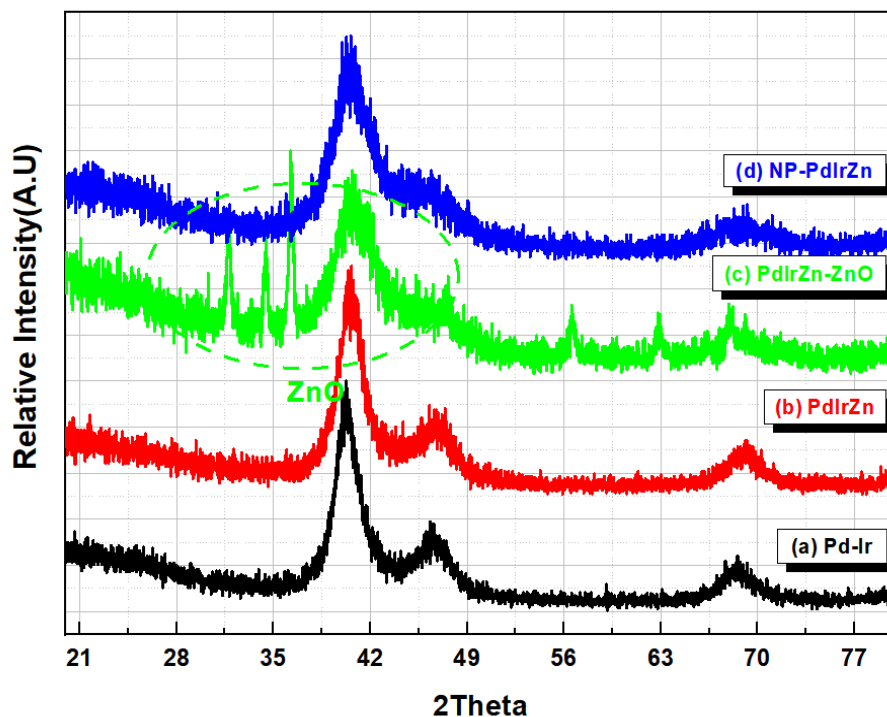


Figure 3. XRD patterns of (a) PdIr, (b) PdIrZn, (c) PdIrZn-ZnO, and (d) NP-PdIrZn catalysts.

Figure 3 shows the XRD patterns of the PdIr alloy catalysts, which were obtained to examine the crystalline structure. The catalysts display a face-centered cubic (fcc) structure similar to that of pure Pd and Ir, showing peaks at 2θ values of 40.0° , 47.0° , and 68.0° , attributed to the (111), (200), and (220)

planes, respectively [33,41,46]. The XRD patterns of the PdIrZn prepared with a smaller amount of the ZnNO_3 precursor do not show peaks ascribable to the ZnO phase, and have peaks at a higher 2θ value of 40.4° compared with that of the PdIr catalyst. This indicates that most Zn atoms were replaced with the Pd or Ir atoms and that the crystal lattice strain occurred due to the smaller size of Zn compared to the Pd and Ir [46–50]. According to Vegard's law, when different metal atoms are alloyed, the crystal lattice changes, causing lattice strain and resulting in peak shifting [46–50].

However, the XRD patterns of the PdIrZn–ZnO nanocomposites prepared using a larger amount of ZnNO_3 precursor can be attributed not only to the hexagonal structure of ZnO (JPDFS card No. 89–1397), but also to the fcc structure of the PdIr alloy in which the Pd or Ir atoms are substituted by Zn atoms (Figure 3c). The XRD patterns of the NP-PdIrZn, obtained by the chemical etching of the PdIrZn–ZnO nanocomposites with 1 M NaOH solution (Figure 3d), show a structure similar to that of the PdIrZn alloy. The mean crystalline sizes of the PdIr, PdIrZn, and NP-PdIrZn particles were estimated to be 3.1, 3.0, and 1.8 nm, respectively. These results indicate that the PdIr-based alloy nanoparticles have multigrain areas. The NP-PdIrZn nanoparticle in particular, has very small grains as the formation of ZnO prevents the growth of the grains in the PdIrZn alloy.

The results of the ICP-AES analyses of the prepared catalysts are shown in Table 1. The average compositions of the PdIr, PdIrZn, PdIrZn–ZnO, and NP-PdIrZn catalysts correspond to atomic ratios of 1:0.84:0, 1:0.90:0.26, 1:0.95:0.91, and 1:0.95:0.27, respectively, for Pd:Ir:Zn with approximately 50 wt.% loading of total metal, which is within the measurement errors. This suggests a homogeneous composition of the sample. The reduction of the Zn content in the NP-PdIrZn confirms the dissolution of ZnO from the PdIrZn–ZnO nanocomposite through selective etching by an NaOH solution.

Table 1. ICP analyses of PdIr, PdIrZn, PdIrZn–ZnO, and NP-PdIrZn catalyst.

Catalyst	Pd (wt.%)	Ir (wt.%)	Zn (wt.%)
PdIr	19.8	30.1	0.0
PdIrZn	19.1	31.0	3.0
PdIrZn–ZnO	18.3	31.5	10.3
NP-PdIrZn	19.7	34.1	3.3

3.2. Electrochemical Properties of Pd Alloy Catalysts

The porous structure formed by the removal of ZnO nanoparticles and the modification of the PdIr alloy using Zn atoms is assumed to change the catalytic activity of the NP-PdIrZn catalysts. To elucidate the relationship between the unique structures of NP-PdIrZn and its ECSA, CV of the PdIr alloy catalysts was recorded in 0.1 M HClO_4 solution in a saturated nitrogen atmosphere (Figure 4). In the CV of the PdIr alloy catalysts, two distinct peaks can be assigned to the adsorption of hydrogen (<0.4 V) and reduction of $\text{Pd}(\text{OH})_2$ (>0.6 V) in the cathodic scan. Compared with the PdIrZn and NP-PdIrZn catalysts, a sharper adsorption peak around 0.05 V is observed in the negative potential scan of the carbon-supported PdIr catalyst, suggesting that Pd is effectively protected from the hydrogen absorption responsible for alloying with Ir [27].

The ECSAs of all the catalysts can be obtained from the total charge of the hydrogen desorption region in the CV, according to methods described elsewhere [39,40]. It is known that the ECSA of an electrocatalyst is the critical parameter representing the electrochemical areas of the exposed metal atoms and the efficiency of the electrochemical reactions. The ECSA increases as follows: PdIr ($49 \text{ m}^2/\text{g}$) < PdIrZn ($71.4 \text{ m}^2/\text{g}$) < NP-PdIrZn ($95.2 \text{ m}^2/\text{g}$). The larger ECSA of the NP-PdIrZn catalyst in comparison with that of the PdIrZn catalyst is associated with a larger number of accessible surface sites for catalytic reaction in the porous structure.

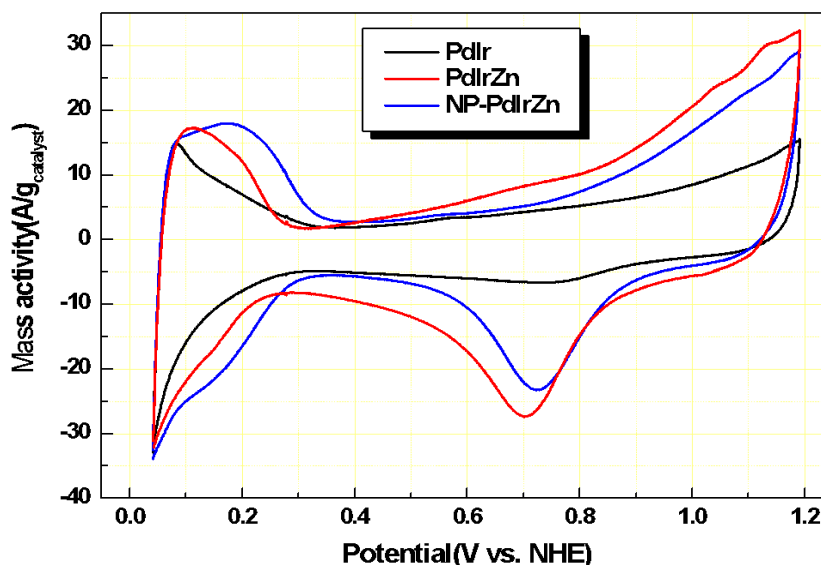


Figure 4. Cyclic voltammograms of PdIr, PdIrZn, and NP-PdIrZn catalysts.

The ECSA appears to depend predominantly on the size of the nanoparticles, with only a negligible contribution from the carbon support [48,51]. Nanoporous materials denote a class of principally desirable ORR catalysts [52,53] as the interconnected frameworks are beneficial for electron transport, while the interconnected pores running through the network facilitate unconstrained gas or water transport. Figure 5 shows the linear scan voltammetry results of all the PdIr-based alloy catalysts in a 0.1 M HClO₄ electrolyte saturated by oxygen at a scan rate of 5 mV/s and 900 rpm, which are used to investigate the relationship of the ORR activity and the nanoporous alloying effect. The mass activity at 0.75 V of the NP-PdIrZn (25.9 A/g) catalyst for the ORR is greater than those of the PdIr (17.8 A/g) and PdIrZn (23.4 A/g) catalysts, which may be ascribed to the nanoporous structure and the strain effect of alloying with Zn in the PdIr catalysts, as suggested by the above results. The mass activity of the NP-PdIrZn catalyst for ORR corresponds to approximately 80% of that from the TKK PtCo catalyst.

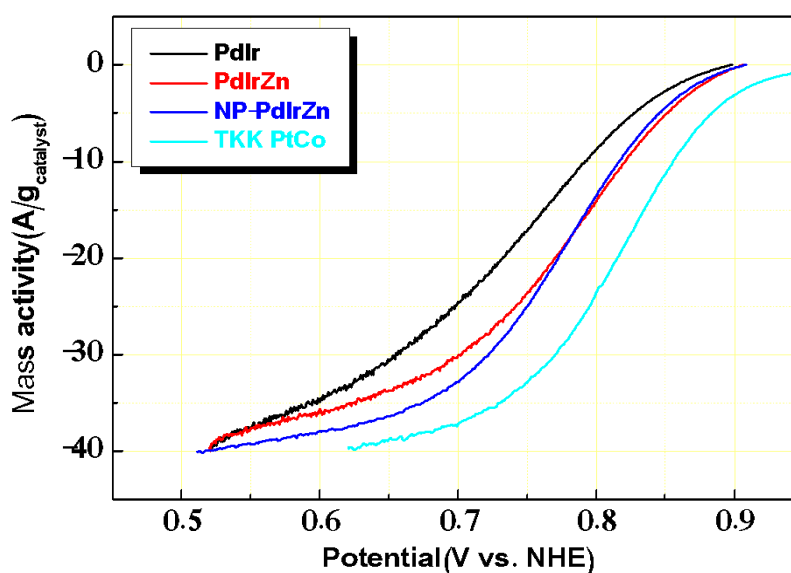


Figure 5. Mass ORR activity of PdIr, PdIrZn, NP-PdIrZn, and TKK PtCo catalysts by linear sweep voltammetry.

To further investigate the impact of the nanoporous alloy on the ORR activity, the PdIr alloy catalysts were grafted to the cathode catalyst layer of the MEA for the HT-PEMFC, and their single-cell

performances we are evaluated (Figure 6 and Table 2). The voltages at 0.2 A/cm^2 are 0.58 V, 0.62 V, 0.66 V, and 0.70 V for the PdIr catalyst, the PdIrZn catalyst, the NP-PdIrZn catalyst, and the PtCo catalyst, respectively, which represents the mixed activation- and Ohmic-controlled voltage of the PEMFC. The cell performance under HT-PEMFC conditions of the NP-PdIrZn catalyst indicates a higher activity than those of the PdIr and PdIrZn catalysts and it is 94.2% of the cell performance of the MEA based on the TKK PtCo catalyst. The NP-PdIrZn/C had a similar performance to the PdNiCu@PdIr/C (0.67 V), which displayed the best single-cell performance among PdIr-based catalysts in previous studies, as listed in Table 2. A difference ($\sim 6\%$) in the performance of the MEA using NP-PdIrZn and PtCo catalysts is decreased compared with the difference ($\sim 20\%$) in the half-cell measurement. This suggests electrode performance is greatly influenced by the fabrication methods for a cathode using the catalysts, and potentially a different poisoning effect on the metal catalyst of the phosphoric acid used particularly for the HT-PEMFC. These data indicate that the improved performance of MEA using a NP-PdIrZn/C catalyst is mainly due to the synergistic combination of the nanoporous structure and the incorporation of Zn in PdIr alloys in the MEA of HT-PEMFCs.

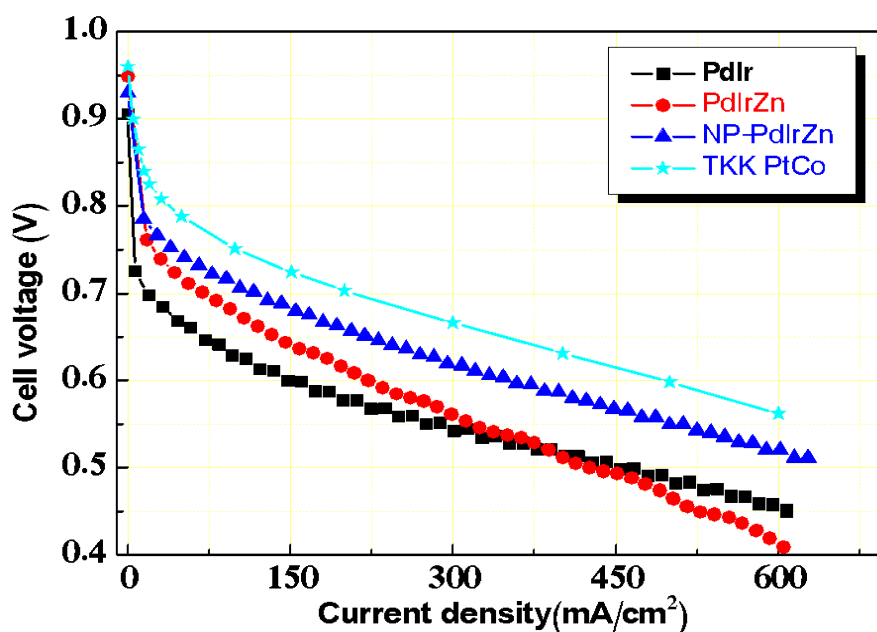


Figure 6. Single-cell performances of PdIr, PdIrZn, NP-PdIrZn, and TKK PtCo catalysts.

Table 2. Single-cell performance of Pd-Ir-based alloy catalysts.

Catalyst	Voltage @ 0.2 A/cm^2 (V)	Reference
PdIr/C	0.58	This work
PdIrZn/C	0.62	This work
NP-PdIrZn/C	0.66	This work
PtCo/C (TKK)	0.70	This work
Ir-PdCu/C	0.53	[27]
PdNi@PdIr/C	0.63	[41]
PdNiCu@PdIr/C	0.67	[41]
PdCu@PdIr/C	0.58	[41]

4. Conclusions

We demonstrated a method for the preparation of an NP-PdIrZn alloy catalyst using the modified alcohol reduction process assisted by microwave heating, resulting in a well-defined nanoporous structure by dissolving the excess metal oxide. The ECSA of the NP-PdIrZn is improved to $95.2 \text{ m}^2/\text{g}$, which is almost twice that of the PdIr catalyst ($49 \text{ m}^2/\text{g}$). The performances of the NP-PdIrZn alloy

catalyst for ORRs and in the single-cell test improved significantly to 0.66 V at 0.2 A/cm² from the 0.58 V and 0.62 V for the PdIr and the PdIrZn, respectively. This is associated with the larger ECSA as a result of the porous structure. The NP-PdIrZn alloy catalyst is a promising candidate that can be used in the future development of Pd-based catalysts for HT-PEMFCs.

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References

1. Liu, Y.; Lehnert, W.; Janßen, H.; Samsun, R.C.; Stolten, D. A review of high-temperature polymer electrolyte membrane fuel-cell (HT-PEMFC)-based auxiliary power units for diesel-powered road vehicles. *J. Power Sour.* **2016**, *311*, 91–102. [[CrossRef](#)]
2. Gurz, M.; Baltacioglu, E.; Hames, Y.; Kaya, K. The meeting of hydrogen and automotive: A review. *Int. J. Hydrogen Energy* **2017**, *42*, 23334–23346. [[CrossRef](#)]
3. Kang, H.S.; Shin, Y.H. Analytical Study of Tri-Generation System Integrated with Thermal Management Using HT-PEMFC Stack. *Energies* **2019**, *12*, 3145. [[CrossRef](#)]
4. Gwak, G.; Kim, M.; Kim, D.; Faizen, M.; Oh, K.; Lee, J.; Choi, J.; Lee, N.; Lim, K.; Ju, H. Performance and Efficiency Analysis of an HT-PEMFC System with an Absorption Chiller for Tri-Generation Applications. *Energies* **2019**, *12*, 905. [[CrossRef](#)]
5. Escorihuela, J.; García-Bernabé, A.; Montero, Á.; Sahuquillo, Ó.; Giménez, E.; Compañ, V. Ionic Liquid Composite Polybenzimidazol Membranes for High Temperature PEMFC Applications. *Polymers* **2019**, *11*, 732. [[CrossRef](#)] [[PubMed](#)]
6. Quartarone, E.; Angioni, S.; Mustarelli, P. Polymer and Composite Membranes for Proton-Conducting, High-Temperature Fuel Cells: A Critical Review. *Materials* **2017**, *10*, 687. [[CrossRef](#)]
7. Hwang, K.; Kim, J.-H.; Kim, S.-Y.; Byun, H. Preparation of Polybenzimidazole-Based Membranes and Their Potential Applications in the Fuel Cell System. *Energies* **2014**, *7*, 1721–1732. [[CrossRef](#)]
8. Kang, R.-J.; Chen, Y.-S. Experimental Study on the Effect of Hydrogen Sulfide on High-Temperature Proton Exchange Membrane Fuel Cells by Using Electrochemical Impedance Spectroscopy. *Catalysts* **2018**, *8*, 441. [[CrossRef](#)]
9. Rosli, R.E.; Sulong, A.B.; Daud, W.R.W.; Zulkifley, M.A.; Husaini, T.; Rosli, M.I.; Majlan, E.H.; Haque, M.A. A review of high-temperature proton exchange membrane fuel cell (HT-PEMFC) system. *Int. J. Hydrogen Energy* **2017**, *42*, 9293–9314. [[CrossRef](#)]
10. Chandan, A.; Hattenberger, M.; El-kharouf, A.; Du, S.; Dhir, A.; Self, V.; Pollet, B.G.; Ingram, A.; Bujalski, W. High Temperature (HT) polymer electrolyte membrane fuel cells (PEMFC)—A review. *J. Power Sour.* **2013**, *231*, 264–278. [[CrossRef](#)]
11. Tang, Y.; Zhang, H.; Zhong, H.; Xu, T.; Jin, H. Carbon-supported Pd–Pt cathode electrocatalysts for proton exchange membrane fuel cells. *J. Power Sour.* **2011**, *196*, 3523–3529. [[CrossRef](#)]
12. Zhou, W.P.; Sasaki, K.; Su, D.; Zhu, Y.; Wang, J.X.; Adzic, R.R. Gram-Scale-Synthesized Pd₂Co-Supported Pt Monolayer Electrocatalysts for Oxygen Reduction Reaction. *J. Phys. Chem. C* **2010**, *114*, 8950–8957. [[CrossRef](#)]
13. Salomé, S.; Ferraria, A.M.; do Rego, A.M.B.; Alcaide, F.; Savadogo, O.; Rego, R. Enhanced activity and durability of novel activated carbon-supported PdSn heat-treated cathode catalyst for polymer electrolyte fuel cells. *Electrochim. Acta* **2016**, *192*, 268–282. [[CrossRef](#)]
14. Chandran, P.; Ghosh, A.; Ramaprabhu, S. High-performance Platinum free oxygen reduction reaction and hydrogen oxidation reaction catalyst in polymer electrolyte membrane fuel cell. *Sci. Rep.* **2018**, *8*, 3591. [[CrossRef](#)] [[PubMed](#)]

15. Seo, M.H.; Choi, S.M.; Lee, D.U.; Kim, W.B.; Chen, Z.W. Correlation between theoretical descriptor and catalytic oxygen reduction activity of graphene supported palladium and palladium alloy electrocatalysts. *J. Power Sour.* **2015**, *300*, 1–9. [[CrossRef](#)]
16. Shao, M. Palladium-based electrocatalysts for hydrogen oxidation and oxygen reduction reactions. *J. Power Sour.* **2011**, *196*, 2433–2444. [[CrossRef](#)]
17. Kariuki, N.N.; Wang, X.; Mawdsley, J.R.; Ferrandon, M.S.; Niyogi, S.G.; Vaughey, J.T.; Myers, D.J. Colloidal Synthesis and Characterization of Carbon-Supported Pd-Cu Nanoparticle Oxygen Reduction Electrocatalysts. *Chem. Mater.* **2010**, *22*, 4144–4152. [[CrossRef](#)]
18. 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](#)]
19. Xu, C.; Zhang, Y.; Wang, L.; Xu, L.; Bian, X.; Ma, H.; Ding, Y. Nanotubular Mesoporous PdCu Bimetallic Electrocatalysts toward Oxygen Reduction Reaction. *Chem. Mater.* **2009**, *21*, 3110–3116. [[CrossRef](#)]
20. Zhao, J.; Sarkar, A.; Manthiram, A. Synthesis and characterization of Pd-Ni nanoalloy electrocatalysts for oxygen reduction reaction in fuel cells. *Electrochim. Acta* **2010**, *55*, 1756–1765. [[CrossRef](#)]
21. Mandal, K.; Bhattacharjee, D.; Roy, P.S.; Bhattacharya, S.K.; Dasgupta, S. Room temperature synthesis of Pd–Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction. *Appl. Catal. A Gen.* **2015**, *492*, 100–106. [[CrossRef](#)]
22. Wang, H.; Wang, C.; Qu, T.; Wang, D.; Kang, Z. Synthesis of Co-Fe-Pd nanoparticles via ultrasonic irradiation and their electro-catalytic activity for oxygen reduction reaction. *Appl. Catal. A Gen.* **2018**, *560*, 103–110. [[CrossRef](#)]
23. Ang, S.-Y.; Walsh, D.A. Palladium–vanadium alloy electrocatalysts for oxygen reduction: Effect of heat treatment on electrocatalytic activity and stability. *Appl. Catal. B Environ.* **2010**, *98*, 49–56. [[CrossRef](#)]
24. Bamos, G.; Kondarides, D.I.; Bebelis, S. Pd–Zn/C bimetallic electrocatalysts for oxygen reduction reaction. *J. Appl. Electrochem.* **2018**, *48*, 675–689. [[CrossRef](#)]
25. Lee, Y.; Jang, J.; Lee, J.G.; Jeon, O.S.; Kim, H.S.; Hwang, H.J.; Shul, Y.G. Optimization of the Pd-Fe-Mo Catalysts for Oxygen Reduction Reaction in Proton-Exchange Membrane Fuel Cells. *Electrochim. Acta* **2016**, *220*, 29–35. [[CrossRef](#)]
26. Yuan, W.; Scott, K.; Cheng, H. Fabrication and evaluation of Pt–Fe alloys as methanol tolerant cathode materials for direct methanol fuel cells. *J. Power Sour.* **2006**, *163*, 323–329. [[CrossRef](#)]
27. You, D.J.; Jin, S.-A.; Lee, K.H.; Pak, C.; Choi, K.H.; Chang, H. Improvement of activity for oxygen reduction reaction by decoration of Ir on PdCu/C catalyst. *Catal. Today* **2012**, *185*, 138–142. [[CrossRef](#)]
28. Yang, T.; Ma, Y.; Huang, Q.; Cao, G. Palladium–iridium nanocrystals for enhancement of electrocatalytic activity toward oxygen reduction reaction. *Nano Energy* **2016**, *19*, 257–268. [[CrossRef](#)]
29. Ham, H.C.; Manogaran, D.; Lee, K.H.; Kwon, K.; Jin, S.-A.; You, D.J.; Pak, C.; Hwang, G.S. Communication: Enhanced oxygen reduction reaction and its underlying mechanism in Pd-Ir-Co trimetallic alloys. *J. Chem. Phys.* **2013**, *139*, 201104. [[CrossRef](#)]
30. Park, S.H.; Choi, C.H.; Koh, J.K.; Pak, C.; Jin, S.-A.; Woo, S.I. Combinatorial High-Throughput Screening for Highly Active Pd–Ir–Ce Based Ternary Catalysts in Electrochemical Oxygen Reduction Reaction. *ACS Comb. Sci.* **2013**, *15*, 572–579. [[CrossRef](#)]
31. Meku, E.; Du, C.; Wang, Y.; Du, L.; Sun, Y.; Kong, F.; Yin, G. Concentration Gradient Pd-Ir-Ni/C Electrocatalyst with Enhanced Activity and Methanol Tolerance for Oxygen Reduction Reaction in Acidic Medium. *Electrochim. Acta* **2016**, *192*, 177–187. [[CrossRef](#)]
32. Meku, E.; Du, C.; Sun, Y.; Du, L.; Wang, Y.; Kong, F.; Yin, G. Composition optimization of ternary palladium–iridium–iron alloy catalysts for oxygen reduction reaction in acid medium. *RSC Adv.* **2016**, *6*, 22754–22763. [[CrossRef](#)]
33. Kim, D.H.; Lee, E.; Pak, C. Comparison of the Characteristics of Pd-Ir-Y Ternary Alloy Catalyst Particles and Oxygen Reduction Activity According to Yttrium Contents. *Trans. Korean Hydrogen New Energy Soc.* **2018**, *29*, 260–266. [[CrossRef](#)]
34. Yang, R.; Bian, W.; Strasser, P.; Toney, M.F. Dealloyed PdCu₃ thin film electrocatalysts for oxygen reduction reaction. *J. Power Sour.* **2013**, *222*, 169–176. [[CrossRef](#)]
35. Zhang, H.; Hao, Q.; Geng, H.; Xu, C. Nanoporous PdCu alloys as highly active and methanol-tolerant oxygen reduction electrocatalysts. *Int. J. Hydrogen Energy* **2013**, *38*, 10029–10038. [[CrossRef](#)]

36. Duan, H.; Xu, C. Nanoporous PdZr surface alloy as highly active non-platinum electrocatalyst toward oxygen reduction reaction with unique structure stability and methanol-tolerance. *J. Power Sour.* **2016**, *316*, 106–113. [\[CrossRef\]](#)
37. Duan, H.; Xu, C. Nanoporous PdCr alloys as highly active electrocatalysts for oxygen reduction reaction. *Phys. Chem. Chem. Phys.* **2016**, *18*, 4166–4173. [\[CrossRef\]](#)
38. Lee, S.W.; Lee, B.H.; Kim, T.-Y.; Baik, C.; Kim, M.S.; Chai, G.S.; Pak, C. Multifunctional non-Pt ternary catalyst for the hydrogen oxidation and oxygen evolution reactions in reversal-tolerant anode. *Catal. Commun.* **2019**, *103*, 105758. [\[CrossRef\]](#)
39. Park, Y.-B.; You, E.; Pak, C.; Min, M. Preparation and characterization of durable catalyst via diazonium reaction in PEMFC. *Electrochim. Acta* **2018**, *284*, 242–252. [\[CrossRef\]](#)
40. Howard, B.H.; Killmeyer, R.P.; Rothenberger, K.S.; Cugini, A.V.; Morreale, B.D.; Enick, R.M.; Bustamante, F. Hydrogen permeance of palladium–copper alloy membranes over a wide range of temperatures and pressures. *J. Membrane Sci.* **2004**, *241*, 207–218. [\[CrossRef\]](#)
41. You, D.J.; Kim, D.H.; De Lile, J.R.; Li, C.; Lee, S.G.; Kim, J.M.; Pak, C. Pd core-shell alloy catalysts for high-temperature polymer electrolyte membrane fuel cells: Effect of the core composition on the activity towards oxygen reduction reactions. *Appl. Catal. A Gen.* **2018**, *562*, 250–257. [\[CrossRef\]](#)
42. Kim, D.-H.; Min, C.-M.; Lee, E.; Lee, J.-S.; Pak, C. Effect of vinylphosphonic acid and polymer binders with phosphate groups on performance of high-temperature polymer electrolyte membrane fuel cell. *Catal. Today* **2019**, in press. [\[CrossRef\]](#)
43. Polarz, S.; Smarsly, B. Nanoporous Materials. *J. Nanosci. Nanotechnol.* **2002**, *2*, 581–612. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Wang, D.; Zhao, P.; Li, Y. General Preparation for Pt-based alloy nanoporous nanoparticles as potential nanocatalysts. *Sci. Rep.* **2011**, *1*, 37. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Erlebacher, J.; Aziz, M.J.; Karma, A.; Dimitrov, N.; Sieradzki, K. Evolution of nanoporosity in dealloying. *Nature* **2001**, *410*, 450–453. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Xu, X.; Wang, X.; Huo, S.; Chen, Z.; Zhao, H.; Xu, J. Facile synthesis of PdIr nanoporous aggregates as highly active electrocatalyst towards methanol and ethylene glycol oxidation. *Catal. Toda* **2018**, *318*, 157–166. [\[CrossRef\]](#)
47. Yi, L.; Wei, W.; Zhao, C.; Yang, C.; Tian, L.; Liu, J.; Wang, X. Electrochemical oxidation of sodium borohydride on carbon supported Pt–Zn nanoparticle bimetallic catalyst and its implications to direct borohydride-hydrogen peroxide fuel cell. *Electrochim. Acta* **2015**, *158*, 209–218. [\[CrossRef\]](#)
48. Behmenyar, G.; Akin, A.N. Investigation of carbon supported Pd–Cu nanoparticles as anode catalysts for direct borohydride fuel cell. *J. Power Sour.* **2014**, *249*, 239–246. [\[CrossRef\]](#)
49. Yogamalar, R.; Srinivasan, R.; Vinu, A.; Ariga, K.; Bose, A.C. X-ray peak broadening analysis in ZnO nanoparticles. *Solid State Comm.* **2009**, *149*, 1919–1923. [\[CrossRef\]](#)
50. Venkateswarlu, K.; Bose, A.C.; Rameshbabu, N. X-ray peak broadening studies of nanocrystalline hydroxyapatite by Williamson–Hall analysis. *Physica B Condens. Matter* **2010**, *405*, 4256–4261. [\[CrossRef\]](#)
51. Stevens, D.A.; Dahn, J.R. Electrochemical Characterization of the Active Surface in Carbon-Supported Platinum Electrocatalysts for PEM Fuel Cells. *J. Electrochem. Soc.* **2003**, *150*, A770–A775. [\[CrossRef\]](#)
52. Corradini, P.G.; Pires, F.I.; Paganin, V.A.; Perez, J.; Antolini, E. Effect of the relationship between particle size, inter-particle distance, and metal loading of carbon supported fuel cell catalysts on their catalytic activity. *J. Nanopart. Res.* **2012**, *14*, 1080. [\[CrossRef\]](#)
53. Yang, R.; Leisch, J.; Strasser, P.; Toney, M.F. Structure of Dealloyed PtCu₃ Thin Films and Catalytic Activity for Oxygen Reduction. *Chem. Mater.* **2010**, *22*, 4712–4720. [\[CrossRef\]](#)

