Intermetallic Pd$_3X$ ($X$= Ti and Zr) nanocrystals for electro-oxidation of alcohols and formic acid in alkaline and acidic media

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**ABSTRACT**

Two highly active and stable Pd-based intermetallic nanocrystals with early d-metals Pd$_3$Ti and Pd$_3$Zr have been developed. The nanocrystals are synthesized by co-reduction of the respective salts of Pd and Ti/Zr. Hard X-ray photoemission Spectroscopy (HAXPES) analysis of the nanocrystals indicates that the electronic properties of Pd are modified significantly, as evident from the lowering of the d-band center of Pd. The intermetallic nanocrystals dispersed in Vulcan carbon, Pd$_3$Ti/C and Pd$_3$Zr/C, exhibit improved electrocatalytic activity towards methanol and ethanol oxidation in an alkaline medium (0.5 M KOH), compared to those of commercially available catalysts such as Pd/C, Pt/C, and Pt$_3$Sn/C. In addition, Pd$_3$Ti/C and Pd$_3$Zr/C show significantly higher activity towards the oxidation of formic acid in an acidic medium (0.5 M H$_2$SO$_4$), compared to those of Pd/C and Pt/C. The modification of the d-band center of Pd as a result of the alloying of Pd with the early d-metals Ti and Zr may be responsible for the enhanced catalytic activity.

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1. Introduction

Direct liquid fuel cells, such as direct alcohol fuel cells (DAFC) and direct formic acid fuel cells (DFAFC), have emerged as a promising energy conversion technology because of their high efficiency and low pollution [1–3]. Pt and Pt-based alloys are the most extensively studied and best catalysts for DAFC and DFAFC [4–8]. However, the use of Pt is limited due to its high cost of Pt, slow reaction kinetics, low stability, and poisoning by CO, which is formed during the electro-oxidation of alcohols or acids [9–13]. Therefore, developing low-cost catalysts with higher activity and stability is of paramount importance for the commercialization of DAFC or DFAFC.

Palladium has attracted increasing attention due to its lower cost, greater abundance, and excellent electrocatalytic activity towards the oxidation of small organic molecules, particularly in alkaline media [14–19]. Alloying Pd with other metals, such as Ag, Au, Sn, Pb, Ni, Cu, etc., is an efficient way to improve the activity of Pd by modifying the structural and electronic properties of the active sites [16,20–30]. Density functional theory (DFT) calculations suggest that the electronic properties of Pd (d-band center) can be modified or even matched with those of Pt by...
alloying the former with early d-metals such as Ti, Zr, and Ta [31,32]. Thus, alloys of Pd with early d-metals are expected to exhibit performances close to or even better than that of Pt in various catalytic reactions. However, developing such alloys is challenging due to the highly oxophilic nature of the early d-metal precursors [33–35]. Herein, we present our attempt to develop a new class of intermetallic nanocrystals consisting of Pd and early d-metals, or Pd$_x$X (where X = Ti and Zr), in addition to detailed characterization of these catalysts. The Pd$_x$X nanocrystals are demonstrated to be efficient catalysts for the oxidation of methanol and ethanol in an alkaline medium. These catalysts also exhibit enhanced catalytic activity toward the oxidation of formic acid, promoting the favorable direct dehydrogenation pathway in an acidic medium. HAXPES measurements suggest that the d-band center of Pd is lowered. The modification of the electronic properties of Pd may be responsible for the enhanced activity of Pd$_x$X nanocrystals in both alkaline and acidic media.

2. Experimental details

2.1 Reagents

We used anhydrous palladium (II) acetate, (Aldrich), anhydrous titanium(IV) chloride tetrahydrofuran complex (TiCl$_4$·2THF, Aldrich,97%), zirconium (IV) chloride (ZrCl$_4$, Aldrich, 99%), diglyme (anhydrous, 99.8%, Aldrich), LiBH$_4$(C$_2$H$_4$)$_2$ (super-hydride, 1 M in THF, Aldrich), hexane (anhydrous, 95%, Aldrich), acetonitrile (99.8%, Aldrich), sodium metal (Aldrich) and naphthalene.

2.2. Synthesis of sodium naphthalide

Sodium naphthalide solution was prepared by dissolving 22.9 mg of metallic sodium and 129.4 mg of naphthalene in dry diglyme. The reaction mixture was stirred overnight under an argon atmosphere.

2.3. Synthesis of Pd$_x$Ti/C NPs

Intermetallic Pd$_x$Ti and NPs were synthesized by co-reduction of the metal precursors in diglyme. Palladium (II) acetate (0.13 mmol) and TiCl$_4$·2THF (0.043 mmol) were weighed and transferred to a round-bottom flask containing the strong reducing agent sodium naphthalide. 54 mg of Vulcan carbon was added to the reaction mixture. The reaction mixture was then transferred to a stainless-steel pressure vessel and heated at 200°C in an oil bath for 2 h under an argon pressure of 0.5 MPa [34,35]. The product was subsequently transferred to a centrifuge tube under an argon atmosphere. The precipitate was separated from diglyme by centrifuging at 6000 rpm for 5 min. The product was washed several times with hexane and acetonitrile to remove the byproducts, and then dried under vacuum for 1 h. The washing solvents were carefully selected to minimize interaction with the oxophilic metal and hence, leaching or dissolution of the metal, resulting in a non-uniform composition. The as-prepared product was annealed at 1000°C for 15 h under vacuum to achieve the desired intermetallic Pd$_x$Ti phase.

2.4. Synthesis of Pd$_x$Zr/C NPs

Intermetallic Pd$_x$Zr NPs were synthesized by co-reduction of the metal precursors in diglyme. Palladium (II) acetate (0.33 mmol) and ZrCl$_4$ (0.11 mmol) were weighed in a stainless-steel pressure vessel. Then, 30 ml of diglyme were added to the vessel, and the mixture was stirred for 20 min to dissolve the reactants. Next, 1 ml of super-hydride was added to the reaction mixture, which was heated at 200°C in an oil bath for 2 h under an argon pressure of 0.5 MPa [34,35]. The product was then transferred to a centrifuge tube under an argon atmosphere. The precipitate was separated from diglyme by centrifuging at 6000 rpm for 5 min. The product was washed several times with hexane and acetonitrile to remove the byproducts and dried under vacuum for 1 h. The as-prepared product was then mixed with Vulcan carbon to form Pd$_x$Zr/C. The as-prepared product Pd$_x$Zr/C was annealed at 1000°C for 15 h under vacuum to obtain intermetallic Pd$_x$Zr/C.

2.5 Synthesis of bulk Pd$_x$Ti and Pd$_x$Zr

Polycrystalline bulk samples of intermetallic Pd$_x$Ti and Pd$_x$Zr were synthesized with an arc furnace in a pure Ar atmosphere (99.9999%). Prior to the synthesis, the arc furnace was evacuated to a vacuum level lower than 10 mPa and back-filled with pure Ar. All of the starting materials were purchased from Furuya Kinzoku Co. An aliquot of 1 g of Pd powder (99.9%) was pelletized with a stainless-steel die and melted into an ingot using an arc furnace. Ti/Zr (ingot, 99%) was used as received. The ingots of Ti/Zr and Pd were weighed such that the molar ratio was Ti/Zr:Pd = 1:3 and melted together in an arc furnace to obtain the desired intermetallic Pd$_x$Ti/Pd$_x$Zr. The product was finally annealed in vacuum at 1000°C for 72 h.

3. Characterization

3.1. Powder X-ray diffractometry (pXRD)

pXRD measurements were performed using Cu Kα radiation (Panalytical X‘Pert PRO; λ = 0.1548 nm) in the range of diffraction angles from 20 to 100 degrees, with increments of 0.02 degrees. An obliquely finished
Si crystal (non-reflection Si plate) was used as a sample holder to minimize the background.

### 3.2. Hard X-ray photoemission spectroscopy (HAXPES)

HAXPES measurements were performed using X-rays with a photon energy of 5.95 keV, at the undulator beamline BL15XU of SPring-8, Japan. Samples for the HAXPES measurements were prepared by mixing the sample solution (in THF) with carbon black (Vulcan XC-72, Cabot Co. Ltd.) to avoid charging effects. 10 µl of the sample was dropped onto a carbon substrate (Nilaco Co., Ltd.) and dried under vacuum. The core-level states of the samples were examined at room temperature in ultrahigh vacuum (UHV) using a hemispherical electron energy analyzer (VG SCIENTA R4000). The total energy resolution was set to 220 meV. The binding energy was referenced to the Fermi edge of an Au thin film.

### 3.3. Transmission electron microscopy

A 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100 F, JEOL) was used. It was equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300 T, JEOL) for compositional analysis. Both the aberration correctors were optimized to realize point-to-point resolutions of 1.3 and 1.1 Å for TEM and scanning transmission electron microscopy (STEM), respectively. A probe convergence angle of 29 mrad and a high-angle annular-dark-field (HAADF) detector with an inner angle greater than 100 mrad were used for HAADF-STEM observation. An UHV-STEM (TECNAI G²) was used to monitor the morphology and particle size of the materials. The samples for UHV-STEM were prepared by dropping a THF suspension of the sample powder onto a commercial TEM grid coated with a colloidal film. The sample was thoroughly dried in vacuum prior to observation.

### 3.4. Electrochemical experiment

Electrochemical measurements were performed with a three-electrode system on a HSV-100 electrochemical apparatus. Ag/AgCl (4 M) and a Pt wire were used as the reference and counter electrodes, respectively. A glassy carbon (GC) electrode (PINE, 5 mm diameter) was polished with Gamma Micropolish Alumina (Batalox, Type 0.05 µm CR) and thoroughly cleaned before use. 4 mg of the catalysts were dispersed in ultrapure water +isopropanol+5% Nafion (v/v/v = 4/1/0.04) with sonication. 45 µl of the suspension was then drop-cast on the cleaned GC electrode and dried at 60°C for 20 min. Prior to the electrochemical measurements, the electrolytes (0.5 M KOH/0.5 M H₂SO₄, Fluka) were degassed by bubbling Ar gas for 30 min. Cyclic voltammetry (CV) measurements were performed at a sweep rate of 20 mV s⁻¹, with 1 M methanol, ethanol and formic acid present in the electrolyte. Commercial Pt/C NPs (20 wt %, Fuel Store) and Pt₃Sn/C (Premetek Co.) were used as the control.

Electrochemical active surface area (ECSA) was obtained from the CV of each of the catalysts in 0.5 M KOH/H₂SO₄ by measuring the coulombic charge obtained from the area under the Pd-O reduction (Q_o) curve, assuming that the charge required for the reduction of Pd-O is 0.405 mC cm⁻², using the following equation [36–38].

$$\text{ECSA} = Q_o / 0.405 \text{mC cm}^{-2}$$

For Pt/C and Pt₃Sn/C, ECSA was calculated using the following equation [39]

$$\text{ECSA} = Q_o / 0.420 \text{mC cm}^{-2}$$

### 4. Results and discussion

Figure 1a presents the powder X-ray diffraction (pXRD) profile of Pd₃Ti/C. The pXRD profile of Pd₃Ti shows intense reflection peaks at 40.2°, 46.7°, 68.3° and 82.3°, corresponding to the 111, 002, 022, and 113 reflections of the face-centered cubic (fcc) structure of Pd. However, these peaks are shifted to higher diffraction angles compared to the reflections of pure Pd, which suggests that the smaller atoms have been incorporated into the fcc crystal lattice of Pd. More importantly, the appearance of the less intense peaks at 22.9°, 32.6°, 52.3° and 58.1° clearly indicates the formation of the intermetallic phase. None of these reflections originates from the fcc-type structure instead from an atomically ordered, intermetallic Pd₃Ti phase. Indeed, the pXRD profiles of Pd₃Ti/C are in good agreement with the simulated pXRD pattern of Pd₃Ti (Cu₃Au structure, Pm3m, a = 3.888 Å) [40]. The atomic arrangements of Pd and Ti in the crystal are shown in Figure 1b. Figure 1c shows the pXRD pattern of Pd₃Zr/C. The pXRD profile of Pd₃Zr/C indicates that the crystal structure of Pd₃Zr is different from the cubic structure of Pd. The peaks at 37.0°, 38.3°, 39.1°, 54.9°, and 63.2° are assigned to the 020, 021, 004, 024, and 025 reflections, respectively, of an atomically ordered intermetallic Pd₃Zr. The experimentally observed pXRD pattern is fully consistent with intermetallic Pd₃Zr with a hexagonal crystal structure (space group P6₃/mmc, a = 5.6119 Å, c = 9.2316 Å, Figure 1d) [41].

HAXPES measurements were used to probe the elemental states of Pd, Ti and Zr in Pd₃Ti/C and Pd₃Zr/C. Figure 2a and b show HAXPES spectra of the core levels
Figure 1. (a) pXRD profile of intermetallic Pd$_3$Ti/C. (b) Structural model showing the atomic arrangement in Pd$_3$Ti. (c,d)pXRD profile of Pd$_3$Zr/C and structural model of intermetallic Pd$_3$Zr. Simulated pXRD profiles of intermetallic Pd$_3$Ti and Pd$_3$Zr are also shown as references.

Figure 2. HAXPES spectra of the Pd 3d- (a) and Ti 2p- (b) regions of the Pd$_3$Ti NPs and those of the Pd 3d- (c) and Zr 3d- (d) regions of the Pd$_3$Zr NPs. HAXPES spectra of the bulk samples of Pd, Ti, Zr, Pd$_3$Ti and Pd$_3$Zr are shown as references.
of Pd and Ti, respectively, in Pd₃Ti NPs. The binding energy (BE) corresponding to the 3d core level of Pd is shifted to a higher energy, indicating the formation of Pd-Ti bonds in Pd₃Ti NPs. This is further confirmed by the shift in the BE of the Ti core level to higher energies (Figure 2b). HAXPES analysis also suggests that a finite amount of oxides of Ti was also present in the Pd₃Ti NPs (Figure S1). A similar trend is observed in the case of Pd₃Zr. The emissions from the core levels, corresponding to the metallic state of Pd and Zr, are shifted to higher energies, indicative of Pd-Zr bonds in the intermetallic compounds (Figures 2c,d, and S1). The composition of the Pd₃Zr NPs was calculated from the intensities of the Pd 3d₅/₂ and Zr 3d₅/₂ emissions as Pd:Zr = 3.0 ± 0.1: 1.2 ± 0.3 [42–45]. The shift of BE to a higher energy arises as a result of the diminished screening of the nuclear charge. The shifts in the BEs of the core levels clearly demonstrate the modification of the electronic structure of Pd, Ti and Zr. The BEs of the core levels of Pd, Ti, and Zr in their respective nanoparticles/bulk samples are tabulated in Tables S1 and S2.

Figure 3a shows a TEM image of Pd₃Ti/C, which consists of spherical particles with a size of 100 nm dispersed on Vulcan carbon. The bigger particles are formed as a result of thermal annealing at high temperature. Selected area electron diffraction (SAED) recorded on an individual nanoparticle is shown in Figure 3b (inset: Pd₃Ti/C nanoparticle). The obtained pattern fits well with the [1 1 0] zone axis, which further supports the pXRD analysis and suggests the formation of Pd₃Ti intermetallic nanoparticles. Energy-dispersive spectroscopy (EDS) combined with TEM was used to determine the distribution of elements as well as the composition of the nanoparticles. As evident from Figure 3c-f, the elements Pd and

![Figure 3](image_url)

**Figure 3.** (a) TEM image and (b) selected area diffraction pattern of Pd₃Ti/C, showing the zone axis of [1 1 0]. (c) STEM image of Pd₃Ti/C. EDS mapping of (d) Pd, (e) Ti and the composite image for the Pd₃Ti/C (f). (g) Size distribution of Pd₃Ti NPs.
Ti are distributed uniformly over the nanoparticles. However, trace amounts of Ti oxides are also observed. Figure 4a shows TEM images of Pd$_3$Zr/C nanoparticles. The average size of the particles is estimated to be 100 nm. The Pd$_3$Zr nanoparticles are uniformly distributed over the carbon matrix. SAED recorded on the single particles matches the [11 0] zone axis (Figure 3b, inset Pd$_3$Zr nanoparticle). The EDS analysis suggests that the distribution of Pd and Zr is uniform within the nanoparticles, with a small amount of oxides on the surface (Figure 4b-e). Compositional analysis with EDS shows that the Pd to Ti/Zr atomic ratio is 3:1 for Pd$_3$Ti/C or Pd$_3$Zr/C (Figures S2, S3).

The electrocatalytic activity of Pd$_3$Ti/C and Pd$_3$Zr/C towards methanol and ethanol oxidation reactions (MOR and EOR, respectively) in alkaline media is tested by CV, and compared with that of commercially available catalysts Pd/C (10 wt %), Pt/C (20 wt %), and Pt$_3$Sn/C (20 wt %). Figure 5a shows the CV curves obtained for the MOR during the forward scan between a potential range from −1.0 V to 0.4 V.

As is evident from Figure 5a, the specific current density of Pd$_3$Ti/C and Pd$_3$Zr/C is 3 and 2.5 times higher, respectively, than that of Pd/C. The current density is obtained by normalizing the current with the electrochemical surface area. It is interesting to note that both Pd$_3$Ti/C and Pd$_3$Zr/C behave similarly, with a slightly higher current density for Pd$_3$Ti/C. The peak maximum for the MOR is shifted to a lower potential compared to that of Pd/C, which suggests that the incorporation of Ti or Zr into Pd facilitates the oxidation of methanol. In other words, the oxidation kinetics of methanol on Pd$_3$Ti/C and Pd$_3$Zr/C are different from those on Pd/C. More importantly, Pd$_3$Ti/C and Pd$_3$Zr/C exhibit a higher specific activity (1.8 times for Pd$_3$Ti/C and 1.6 times for Pd$_3$Zr/C) in comparison with that of Pt/C. Compared with Pd/C and

Figure 4. (a) TEM image and (b) selected area diffraction pattern of Pd$_3$Zr/C, showing the [1 1 0] zone axis. (c) STEM image of Pd$_3$Zr/C. EDS mapping of (d) Pd, (e) Zr and the composite image for the Pd$_3$Zr/C (f) are also shown. (g) The statistical distribution of Pd$_3$Zr NPs.
Pt/C, the lower oxidation peak potential and higher oxidation current density indicate that Pd$_3$Ti/C and Pd$_3$Zr/C can be considered as promising candidates for the MOR. The long-term stability and activity of Pd$_3$Ti/C and Pd$_3$Zr/C for the MOR was tested by chronoamperometry at −0.2 V. The intermetallic compounds show a higher current density compared to that of Pd/C for 3600 s (Figure S4). The reproducible operation of the catalysts was further verified by accelerated durability tests (ADT) at a scan rate of 90 mVs$^{-1}$. The durability was tested by comparing the peak current density for different potential cycles (Figures 5b, S5). As is evident from Figure 5b, the current density remains virtually the same even after 300 potential cycles for Pd$_3$Ti/C and Pd$_3$Zr/C. However, Pd/C and Pt/C lose ~40% to 50% of the initial current density after 300 cycles (Figure S5).

Figure 6a shows the CV curves of the EOR on different catalysts. The specific current density for Pd$_3$Ti/C and Pd$_3$Zr/C is 2.35 and 2.25 times higher, respectively, than that of Pd/C. In addition, the onset potential for Pd$_3$Ti/C (−0.574 V) and Pd$_3$Zr/C (−0.521 V) is shifted to a significantly lower potential in comparison with that of Pd/C (−0.480 V). Importantly, the oxidation peak potential of the EOR shifts by −0.175 V for Pd$_3$Ti/C and −0.125 V for Pd$_3$Zr/C, in comparison with that of Pd/C (0 V). It should be noted that the activity of Pd$_3$Ti/C and Pd$_3$Zr/C towards the EOR is remarkably higher than that of Pt/C and Pd$_3$Sn/C. Considering the onset potential, current density, and oxidation peak potential, Pd$_3$Ti/C is found to be the best catalyst for the EOR. Note that the oxidation peaks for the MOR and EOR over the Pd$_3$Ti- and Pd$_3$Zr catalysts were narrow and sharp compared to those for the control materials, Pd/C, Pt/C or Pd$_3$Sn/C, reflecting that the surface Pd atoms are surrounded by the Ti- and Zr-atoms to act as an isolated adsorption centre for the reaction intermediate, CO.

Chronoamperometry measurements at −0.2 V show that Pd$_3$Ti/C and Pd$_3$Zr/C are superior to Pd/C, exhibiting a higher current density for 600 s (Figure S6), indicating a higher tolerance of Pd$_3$Ti/C and Pd$_3$Zr/C to the carbonaceous species generated during ethanol oxidation. The durability of the catalysts in the EOR was further tested with ADT at a scan rate of 90 mVs$^{-1}$ (Figure 6b). The current density of Pd$_3$Ti/C and Pd$_3$Zr/C increases with an increasing number of
Figure 6. (a) CV curves of ethanol oxidation on different catalysts in 1 M ethanol + 0.5 M KOH at a scan rate of 20 mVs⁻¹. (b) Variation of normalized current density at the peak maximum of different potential cycles from the first to the 300th cycle of ethanol oxidation.

potential cycles and then remains constant, even after 300 ADT cycles. However, the activity of Pd/C and Pt/C is decreased by 40% after 300 cycles (Figure S7). Therefore, the above results demonstrate that Pd₃Ti/C and Pd₃Zr/C show improved catalytic activity and stability in reproducible operation for the EOR.

We further tested the activities of the catalysts towards formic acid electro-oxidation (FAEO) in an acidic medium (Figure 7a). Pd-based catalysts are known to facilitate the oxidation of formic acid through the dehydrogenation pathway. The peak current intensity for Pd₃Ti/C and Pd₃Zr/C is 6.8 and 3.5 times higher, respectively, than that of Pd/C. The onset potential of Pd₃Ti/C (−0.118 V) is much more negative than that of Pd₃Zr/C (−0.04 V) and Pd/C (−0.07 V).

The ADT experiments finally suggest that Pd₃Ti/C exhibits very good tolerance to repeated operation towards formic acid oxidation. For Pd₃Ti/C, the current density initially increases with the number of cycles and remains constant even after 200 cycles (104%). However, the activity of Pd₃Zr/C is decreased with an increasing number of cycles (35% loss) after 200 cycles. On the other hand, Pd/C loses almost 90% of its initial activity within even 100 potential cycles, which suggests that alloying of Pd with Ti/Zr improves the stability of the catalysts (Figure 7b). The superior stability of Pd₃Ti/C to Pd₃Zr/C may be attributed to the chemical stability of titanium oxides (TiOₓ) layers on the catalyst surface (Figure S1), which can inhibit surface segregation or dealloying in acidic electrolytes.

The d-band centers of Pd₃Ti- and Pd₃Zr NPs were calculated as −3.47 eV and −3.71 eV, respectively. These values are lowered significantly compared to that of pure Pd, which is close to −3.10. More importantly, the d-band centers of Pd₃Ti- and Pd₃Zr NPs are even lower than that of Pt, −3.31 eV (Figure S8). The lowered d-band center of PdₓX can alter hybridization strength of one of the major reaction intermediates of FAEO, MOR and EOR, carbon monoxide that works a catalytic poison,
which may result in the improved electrocatalytic performances.

5. Conclusion

We have developed two Pd-based inter-metallic nanocrystals with the early d-metals Ti and Zr. The Pd$_3$Ti/C and Pd$_3$Zr/C catalysts were characterized in detail using pXRD, TEM and EDS. These newly developed catalysts exhibit enhanced catalytic activity towards methanol and ethanol electro-oxidation in an alkaline medium and formic acid electro-oxidation in an acidic medium, compared to commercially available catalysts.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supporting information

Synthesis, characterization (pXRD, HAXPES, TEM) and electrochemical data.

References

[1] Arico AS, Bruce P, Scrosati B, et al. Nanostructured materials for advanced energy conversion and storage devices. Nat Mater. 2005;4:366–377.
[2] Debe MK. Electrocatalyst approaches and challenges for automotive fuel cells. Nature. 2012;486:43–51.

[3] Kakati N, Maiti J, Lee SH, et al. Anode catalysts for direct methanol fuel cells in acidic media: do we have any alternative for Pt or Pt–Ru? Chem Rev. 2014;114:12397–12429.

[4] Stamenkovic VR, Fowler B, Mun BS, et al. Improved oxygen reduction activity on Pt3Ni(111) via increased surface site availability. Science. 2007;315:493–497.

[5] Lamy C, Belgir EM, Leger JM. Electrocatlytic oxidation of aliphatic alcohols: application to the direct alcohol fuel cell (DAFC). J Appl Electrochem. 2001;31:799–809.

[6] Lamy C, Lima A, LeRuhn V, et al. Recent advances in the development of direct alcohol fuel cells (DAFC). J Power Sources. 2002;105:283–296.

[7] Yu X, Pickup PG. Recent advances in direct formic acid fuel cells (DAFC). J Power Sources. 2008;182:124–132.

[8] Choi JH, Jeong KJ, Dong Y, et al. Electro-oxidation of methanol and formic acid on PtRu And PtAu for direct liquid fuel cells. J Power Sources. 2006;163:71–75.

[9] Yu W, Porosoff MD, Chen JG. Review of Pt-based bimetallic catalysis: from model surfaces to supported catalysts. Chem Rev. 2012;112:5780–5817.

[10] Kavanagh R, Cao XM, Lin WP, et al. Origin of low CO2 selectivity on platinum in the direct ethanol fuel cell. Angew Chem Int Ed. 2012;51:1572–1575.

[11] Silva JCM, Parreira LS, De Souza RFB, et al. PtSn/C alloyed and non-alloyed materials: differences in the ethanol electro-oxidation reaction pathways. Appl Catal B. 2013;110:141–147.

[12] Lima FHB, Gonzalez ER. Ethanol electro-oxidation on carbon-supported Pt–Ru, Pt–Rh and Pt–Ru–Rh nanoparticles. Electrochim Acta. 2008;53:2963–2971.

[13] Wang Q, Sun GQ, Jiang LH, et al. Adsorption and oxidation of ethanol on colloidal-based Pt/C, PtRu/C and PtSn/C catalysts: in situ FTIR spectroscopy and online DEMS studies. Phys.Chem.Chem.Phys. 2007;9:2686–2696.

[14] Hu G, Nitze F, Gracia-Espino E, et al. Small palladium islands embedded in palladium–tungsten bimetallic nanopores form catalytic hotspots for oxygen reduction. Nat Commun. 2014;5(2525):1–9.

[15] Zhu C, Guo S, Dong S. PdM (M = Pt, Au) Bimetal alloy nanowires with enhanced electrocatlytic activity for electro-oxidation of small molecules. Adv Mater. 2012;24:2326–2331.

[16] Mazumder V, Chi M, Mankin MN, et al. A facile synthesis of MPd (M = Co, Cu) nanoparticles and their catalysis for formic acid oxidation. Nano Lett. 2012;12:1102–1106.

[17] Liu W, Herrmann K, Geiger D, et al. High performance electrocatalysis on palladium aerogels. Angew Chem Int Ed. 2012;51:5743–5747.

[18] Wu H, Li H, Zhai Y, et al. Facile synthesis of free-standing Pd-based nanomembranes with enhanced catalytic performance for methanol/ethanol oxidation. Adv Mater. 2012;24:1594–1597.

[19] Yin S, Cai M, Wang C, et al. Tungsten carbide promoted Pd–Fe as Alcohol-tolerant electrocatalysts for oxygen reduction reaction. Energy Environ Sci. 2011;4:558–563.

[20] Bianchini C, Shen PK. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. Chem Rev. 2009;109:4183–4206.

[21] Liu D, Guo Q, Hou H, et al. PdxCoy nanoparticle/carbon nanofiber composites with enhanced electrocatalytic properties. ACS Catal. 2014;4:1825–1829.

[22] She Y, Lu Z, Fan W, et al. Facile preparation of PdNi/rGO and its electrocatalytic performance towards formic acid oxidation. MaterChemA. 2014;2:3894–3898.

[23] Cui Z, Yang M, DiSalvo FJ. Mesoporous Ti83Cu17 N supported PdAgNanooalloy as highly active and stable catalysts for the electro-oxidation of formic acid and methanol. ACS Nano. 2014;8:6106–6113.

[24] Mao H, Huang T, Yu AS. Facile synthesis of trime- tallic Cu3Au10Pt14/C catalyst for ethanol oxidation with superior activity and stability. J Mater Chem A. 2014;2:16378–16380.

[25] Lu Y, Jiang Y, Gao X, et al. Strongly coupled Pd nanotetrahedron/tungsten oxide nanosheet hybrids with enhanced catalytic activity and stability as oxygen reduction electrocatalysts. J Am Chem Soc. 2014;136:11667–11697.

[26] Fu S, Zhu C, Du D, et al. Facile one-step synthesis of three-dimensional Pd–Ag bimetallic alloy networks and their electrocatalytic activity toward ethanol oxidation. ACS Appl Mater Interfaces. 2015;7:13842–13848.

[27] Luo Y, Jiang Y, Chena W. Pt Pd porous nanorods with enhanced electrocatalytic activity and durability for oxygen reduction reaction. Nano Energy. 2013;2:836–844.

[28] Liu M, Lu Y, Chen W. Pd Ag Nanorings supported on graphene nanosheets: highly methanol-tolerant cathode electrocatalyst for alkaline fuel cells. Adv Funct Mater. 2013;23:1289–1296.

[29] Zhang Z, Zhang C, Sun J, et al. Ultrasfine nanoporous PdFe/Fe3O4 catalysts with doubly enhanced activities towards electro-oxidation of methanol and ethanol in alkaline media. J Mater Chem A. 2013;1:3620–3628.

[30] Qia Z, Gengh H, Wanga X, et al. Novel nanocrystalline PdNi Alloy catalyst for methanol and ethanol electro-oxidation in alkaline media. J Power Sources. 2011;196:5823–5828.

[31] Shao M, Liu P, Zhang J, et al. Origin of enhanced activity in palladium alloy electrocatalysts for oxygen reduction reaction. J PhysChemB. 2007;111:6772–6775.

[32] Yu TH, Sha Y, Merinov BV, et al. Improved non-Pt alloys for the oxygen reduction reaction at fuel cell cathodes predicted from quantum mechanics. J Phys ChemC. 2010;114:11527–11533.

[33] Abe H, Matsumoto F, Alden LR, et al. Electrocatlytic performance of fuel oxidation by Pt3Ti nanoparticles. J Am Chem Soc. 2008;130:5452–5458.

[34] Ramesh GV, Kodiyath R, Tanabe T, et al. NbPt3 intermetallic nanoparticles: highly stable and CO-tolerant electrocatalyst for fuel oxidation. ChemElectroChem. 2014;1:728–732.

[35] Ramesh GV, Kodiyath R, Tanabe T, et al. Stimulation of electro-oxidation catalysis by bulk-structural transformation in intermetallic ZrPt3 nanoparticles. ACS Appl Mater Interfaces. 2014;6:16124–16130.

[36] Zhang Z, More KL, Sun K, et al. Preparation and characterization of PdFeNanoleaves as electrocatalysts for oxygen reduction reaction. Chem Mater. 2011;23:1570–1577.

[37] Jiang L, Hsu A, Chu D, et al. Oxygen reduction reaction on carbon supported Pt and Pd in alkaline solutions. J Electrochem Soc. 2009;156(3):B370–B376.
Singh RN, Singh A. Anindita, electrocatalytic activity of binary and ternary composite films of Pd, MWCNT and Ni, Part II: methanol electrooxidation in 1 M KOH. Int J Hydrogen Energy. 2009;34:2052–2057.

Kodiyath R, Ramesh GV, Koudelkova E, et al. Promoted C–C bond cleavage over intermetallic TaPt₃ catalyst toward low-temperature energy extraction from ethanol. Energy Environ Sci. 2015;8:1685–1689.

Evans J, Harris IR, Guzei LS. An investigation of some palladium-titanium and some palladium-titanium-hydrogen alloys. J Less-Common Met. 1979;4:39–57.

Harris IR, Norman M. Observations on the lattice spacings of some α Pd-X solid solutions and some PdₓX phases. J Less-Common Met. 1970;22:127–130.

Yeh JJ, Lindau I. Atomic subshell photoionization cross sections and asymmetry parameters: 1 < Z < 103. Atomic Data Nucl Data Tables. 1985;32:1–155.

Scofield, J H. Mon. “Theoretical photoionization cross sections from 1 to 1500 keV”. United States. doi:10.2172/4545040. https://www.osti.gov/servlets/purl/4545040.

Trzhaskovskaya MB, Nefedov VI, Yarzhemsky VG. Photoelectron angular distribution parameters for elements Z=1 to Z=54 in the photoelectron energy range 100–5000 eV. Atomic Data Nucl Data Tables. 2001;77:97–159.

Trzhaskovskaya MB, Nikulin VK, Nefedov VI, et al. Non-dipole second order parameters of the photoelectron angular distribution for elements Z=1–100 in the photoelectron energy range 1–10keV. Atomic Data Nucl Data Tables. 2006;92:245–304.