

# Pd-Based Electrocatalysts for Oxygen Reduction and Ethanol Oxidation Reactions: Some Recent Insights into Structures and Mechanisms

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**Abstract:** The development of efficient electrocatalysts for applications in fuel cells, including proton-exchange membrane fuel cell (PEMFC) and direct ethanol fuel cell (DEFC), has attracted extensive research attention in recent years. Oxygen reduction reaction and ethanol oxidation reaction are two of the key reactions where the design of active, stable and low-cost electrocatalysts is critical for the mass commercializations of PEMFCs and DEFCs. This challenge stems largely from the limited understanding of the catalyst structures and reaction mechanisms. Progress has been made in investigations of electrocatalysts derived from Pd-based alloy nanomaterials both experimentally and computationally. We highlight herein some of the recent insights into the catalyst structures and reaction mechanisms of Pd and Pd-based electrocatalysts in oxygen reduction reaction and ethanol oxidation reaction. Both experimental and computational aspects will be discussed, along with their implications for the design of optimal electrocatalysts.

**Key words:** oxygen reduction reaction; ethanol oxidation reaction; electrocatalyst; phase structure; reaction mechanism; fuel cells

## 1 Introduction

The development of proton-exchange membrane fuel cells (PEMFCs) and direct ethanol fuel cells (DEFCs) represents an important vector in the global drive seeking sustainable and highly efficient energy sources for automobiles and electronic devices. A great deal of interests has been attracted to both fundamental researches and industrial applications of PEMFCs and DEFCs due to their high theoretical mass energy density, nontoxicity, convenient fuel storage, and abundant renewable ethanol source<sup>[1-3]</sup>. Significant progress has been made in the develop-

ment of electrocatalysts for PEMFCs and DEFCs, focusing on the oxygen reduction reaction (ORR) at the cathode and the ethanol oxidation reaction (EOR) at the anode<sup>[4-7]</sup>. However, one of the major challenges stems largely from limited fundamental understanding of the detailed reaction mechanism and structure-activity correlation for ORR and EOR electrocatalysts.

Pt- and Pd-based electrocatalysts have been one of the most important focal points of research and development. There have been many recent reviews focusing on Pt-based electrocatalysts<sup>[8,9]</sup>. Pd-based nanoma-

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terials, as an important part of the nanomaterials derived from platinum group metals, have attracted increasing interest as a potential group of efficient and promising fuel cell electrocatalysts<sup>[2, 4, 5, 10-12]</sup>. We focus on some of the recent developments in structural and mechanistic characterizations of Pd-based electrocatalysts for ORR and EOR in this article. Computational investigations involving density functional theory (DFT) studies and Reverse Monte Carlo (RMC) simulations have been gaining increasing importance in aiding structural predictions and mechanistic explanations<sup>[2, 3, 10, 13-20]</sup>. The dynamic nature of nanoalloys under the reaction conditions has been recognized for the characterization of the catalysts in fuel cell reactions<sup>[8, 9]</sup>. In comparison with Pt-based catalysts, the unique dynamic evolution of Pd-based catalysts has captured increasing interests for the fundamental understanding. We will highlight some recent examples which combine experimental and computational approaches to unravel the structure-activity correlations of Pd and Pd-based electrocatalysts in fuel cell reactions, focusing on ORR and EOR.

## 2 Oxygen Reduction Reaction

For ORR, the reaction involves breaking the oxygen-oxygen double bond of dioxygen molecule, the activation of which depends on the catalyst's surface sites for O<sub>2</sub> dissociative adsorption. As such, the electrocatalytic activity and stability of nanostructured alloy catalysts depend strongly on the detailed phase structures. Pd and Pd-based nanomaterials have been widely studied as ORR electrocatalysts<sup>[8, 15, 21, 22]</sup>. The catalytic synergy in binary and multimetallic Pd-based alloy nanomaterials enables great performance enhancement comparing with Pd nanomaterials in a similar morphology<sup>[15, 22]</sup>. In this section, we will highlight some recent findings in the studies of Pd-based bimetallic/multimetallic alloy ORR catalysts, e.g., PdCu, PdSn, and PdPt nanoparticle catalysts.

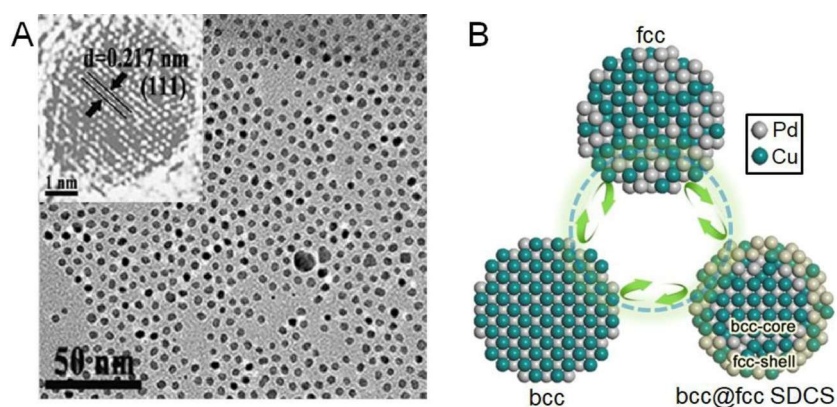
### 2.1 PdCu

The first example involves PdCu nanoparticle catalysts for ORR. The ORR activity depends heavily on the elemental combination/composition and the

phase structure of Pd-based alloy electrocatalysts. For example, the best ORR activity of PdCu nanoparticles was achieved with a Pd/Cu ratio of 1:1<sup>[22]</sup>, where the lowest activation barrier of O<sub>2</sub> bond breaking, and the weakest adsorption energies of \*OH, \*O, and \*OOH were demonstrated by DFT calculations at this ratio<sup>[23]</sup>. The catalytic synergy between Pd and Cu observed experimentally was demonstrated by DFT calculations<sup>[13, 15]</sup>. The addition of Cu in PdCu alloy lowers the d-band center of Pd toward the peak of the volcano plot and hence boosts the ORR activity. These findings agree well with the composition-activity relationship and the catalytic synergy of multimetallic Pd-based alloy ORR catalysts revealed in recent studies<sup>[22, 24]</sup>.

However, the structure-activity correlation for ORR, especially with different phase structures, while is very important, but also remains unclear. This has been recently demonstrated by a set of systematic studies on PdCu nanoparticle ORR electrocatalyst<sup>[15, 25]</sup>. As shown in Figure 1, PdCu alloy nanoparticles with a uniform size distribution (Figure 1(A)) are likely to be shown in different phase structures, i.e., face-centered cubic (fcc) and body-centered cubic (bcc), or fcc/bcc mixed phase structure (Figure 1(B)). The phase structure is highly tunable by the wet chemical synthesis approach<sup>[26]</sup> and the thermochemical calcination at varying temperatures<sup>[15]</sup>. Thermochemical treatment is a widely used approach to remove the organic capping agents, while reconstructing the structure of alloy nanomaterials toward a thermochemically stable state at a certain temperature<sup>[27]</sup>. The in-depth understanding of the role of thermochemical treatment, especially under different gas atmospheres (e.g., H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, NH<sub>3</sub>, etc.) and treatment temperatures, in tuning the structures and catalytic performance of the nanomaterials is part of current investigations.

In fact, detailed insights into the nanophase structures of nanomaterials can be obtained by X-ray diffraction (XRD) and high-energy XRD (HE-XRD) techniques. As shown in Figure 2, PdCu nanoparticles with an initial random alloy structure could be reconstructed to a pure fcc structure at the annealing

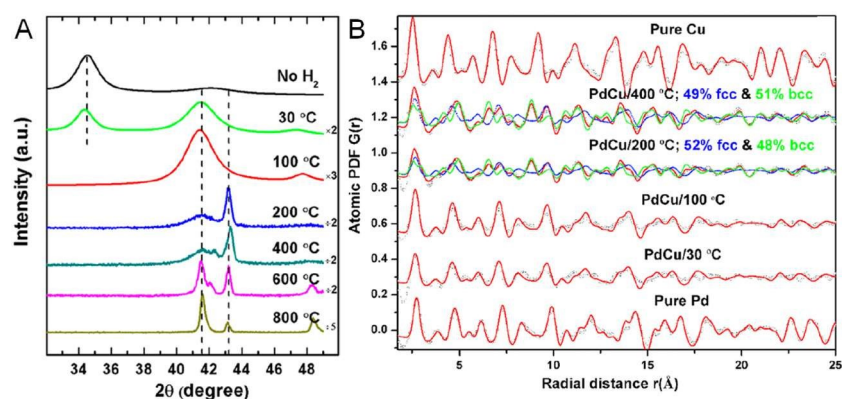


**Figure 1** (A) A representative transmission electron microscopic (TEM) image (the inset is a representative high-resolution TEM image) of PdCu nanoparticles; (B) A schematic illustration of fcc/bcc phase structure evolution for PdCu nanoparticles<sup>[15]</sup>.

temperature of 100 °C (PdCu/100 °C) under reducing gas atmosphere ( $H_2/N_2$ ), and to a mixture of fcc and bcc structure at 200 °C ~ 800 °C in the same annealing condition. Furthermore, HE-XRD technique is able to determine the exact percentage of each type of phase structure. Note that the regular XRD characterization could provide some preliminary information about the phase structure content of nanoparticles with relatively larger sizes (typically > 2 nm) by analyzing the corresponding major diffraction peak areas.

HE-XRD technique coupled with pair distribution function (PDF) analyses and RMC simulations provides an in-depth decipher of the detail structure information of nanomaterials<sup>[8]</sup>. Herein, *in-situ* synchrotron HE-XRD experiments were carried out on a custom designed PEMFC with the target ORR cata-

lysts loaded on the cathode side. The synchrotron X-rays penetrate through the PEMFC and the HE-XRD patterns are collected by a panel detector. The collected HE-XRD data are analyzed by PDFs and RMC simulations, which are able to provide abundant structure information such as phase structure types and contents, lattice parameters/strains, coordination numbers, and atomic distances. Demonstrated by HE-XRD/PDF/RMC techniques, PdCu/100 °C exhibits a composition-homogeneous alloy and pure fcc structure, while PdCu/400 °C shows a structurally different core-shell type with bcc-core and fcc-shell rather than other structures such as fcc-type random alloy, fcc-type alloy with Pd-rich surface, Janus-type, pure Cu core@pure Pd shell, pure Pd core@Cu shell, Pd-Cu-Pd sandwich, bcc alloy, etc. (Figure 3)<sup>[25]</sup>. Remarkably, the HE-XRD/PDF/RMC



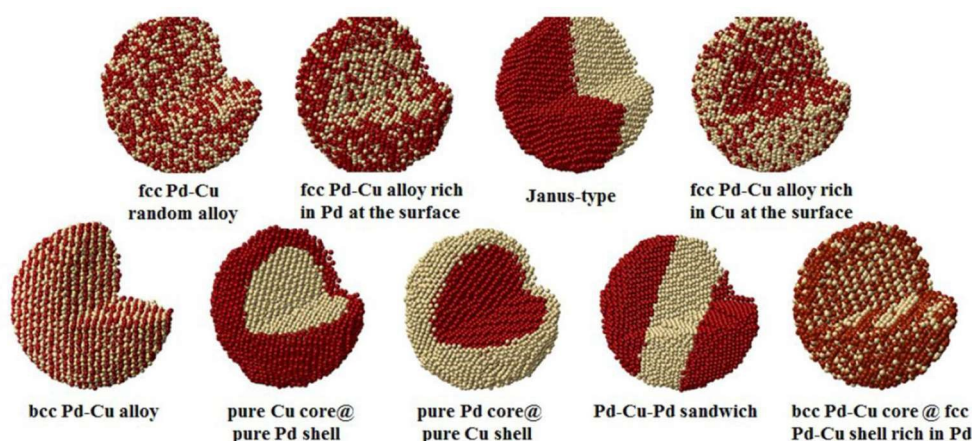
**Figure 2** (A) XRD patterns and (B) atomic PDFs for PdCu/C nanoparticles thermochemically treated at different temperatures<sup>[15]</sup>. (color on line)

techniques provide detailed structures of the nanostructured catalysts, especially under *in-situ/operando* operating conditions, by capturing the dynamic structure evolution, as recently highlighted in some of our recent reports and reviews<sup>[8, 9, 18, 19, 21]</sup>.

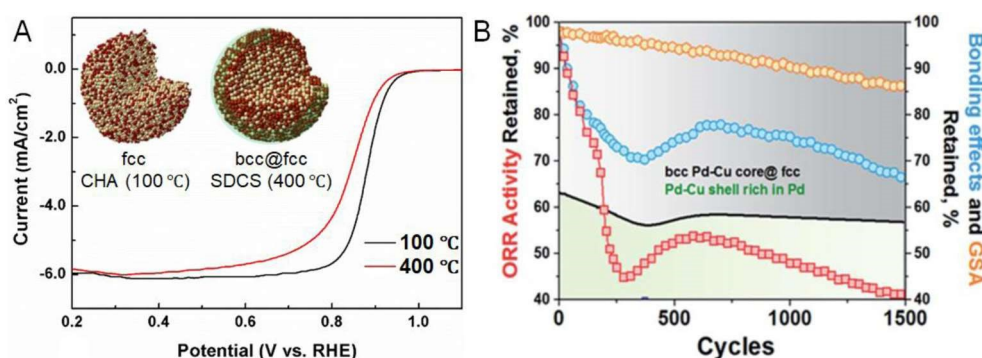
The elevated calcination temperature ( $> 200\text{ }^{\circ}\text{C}$ ) is believed to enable a phase reconstruction process mainly in the core region of PdCu nanoparticles to a thermodynamically-stable state, i.e., from fcc to bcc. A correlation between phase structure and ORR activity was established (Figure 4(A)). PdCu/100  $^{\circ}\text{C}$  with a pure fcc structure showed a much higher ORR mass activity than PdCu/400  $^{\circ}\text{C}$  with a fcc/bcc mixed phase structure. The *in-situ* HE-XRD/PEMFC experiment could track the dynamic structure evolution process along with the potential cycling (Figure 4(B)). The

results demonstrated a quick ORR activity decay in the first few hundreds of potential cycles, and followed by an activity recovery before a further gradual decrease. The trend of ORR activity correlates well with the trend of the bonding effect, i.e., strain and ligand contributions. Finally, RMC simulation revealed a well maintenance of such bcc-core@fcc-shell structure of PdCu/400  $^{\circ}\text{C}$  after 1,500 potential cycles, demonstrating its phase structure stability. Note that the phase structure stability of PdCu nanoalloy is in sharp contrast to other Pd-based nanoalloys, e.g., PdSn. PdSn nanoalloys show a quick phase structure evolution upon potential cycling, which will be discussed later.

DFT calculations provide mechanistic insights into ORR reaction on the catalyst surfaces and thus aid



**Figure 3** RMC models with varying phase structures of PdCu nanoparticle. Yellow and red balls are Cu and Pd atoms, respectively<sup>[25]</sup>. (color on line)



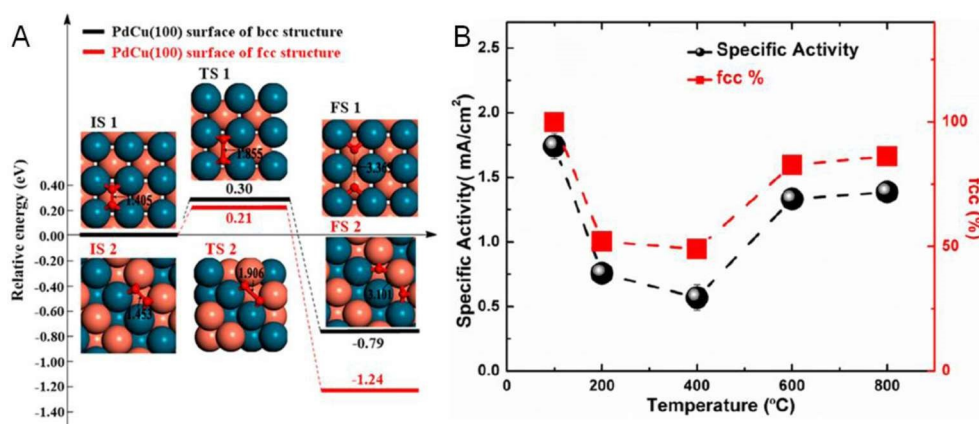
**Figure 4** (A) RDE curves of different PdCu/C catalysts. Insets are the corresponding RMC models featuring different structures; (B) Evolution of the bonding effects, geometric surface area, and retained ORR activity along with the potential cycling numbers for Pd-Cu/400  $^{\circ}\text{C}$  catalyst in the *in-situ* HE-XRD/PEMFC experiment<sup>[15, 25]</sup>. (color on line)

the understanding of the structure-activity correlation. As shown in Figure 5(A), an fcc-structured PdCu model showed a lower reaction barrier of the  $O_2$  cleavage step comparing with a bcc-structured counterpart. A highly consistent trend was observed between the fcc percentage in PdCu/C nanoparticles and the corresponding ORR specific activity (Figure 5(B)). This might indicate that PdCu nanomaterials with fcc phase structure could exhibit better intrinsic ORR activity than the bcc-structured counterpart. Rigorously, such comparison in the experiment should be based on two nanomaterials with pure fcc and pure bcc structures, respectively<sup>[26]</sup>, which calls for further explorations. The reaction mechanism of ORR is complex as it is a multi-electron transfer reaction and involves in a three-phase heterogeneous interface. Many of the current theoretical calculations involved highly-simplified models and might not represent the major factor for assessing the ORR. The study of the solvent effect by including both explicit (by introducing surface  $H_2O$  and  $OH$  species in the model) and implicit (by considering dielectric constants of solvents) models has gained increasing attentions. The analysis of the reaction kinetics by including the reaction barriers for key elementary steps in ORR has being widely considered in DFT calculations.

## 2.2 PdSn

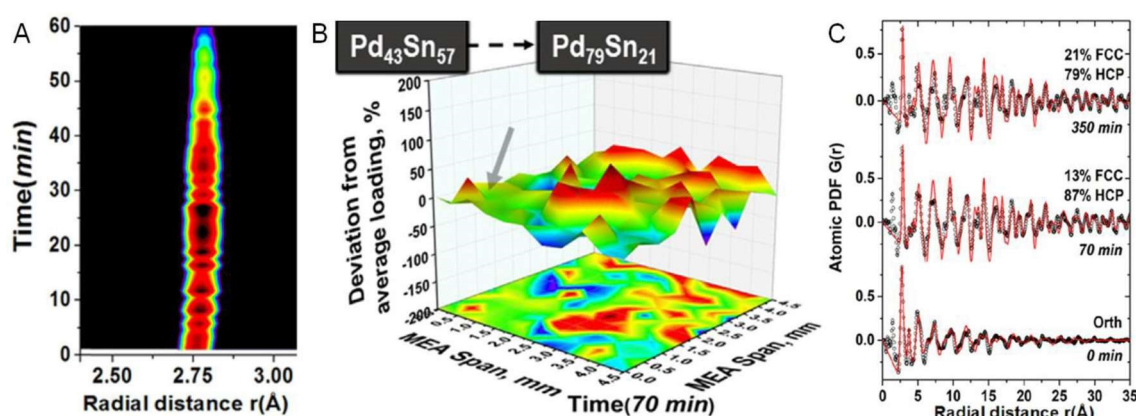
Another interesting study involves PdSn alloy nanoparticle electrocatalysts<sup>[28]</sup>. For a typical  $Pd_{43}Sn_{57}$

nanoparticle catalyst, the dynamic lattice constant evolution under the *in-situ* fuel cell operating condition was exemplified by a color map of the first atomic PDF peak (Figure 6(A)). The fluctuation of the lattice constant is indicative of an intriguing oscillatory kinetics, which can be attributed to the dealloying-re alloying nature of such dynamic evolution process during the potential cycling operation as recently substantiated by a PtPdCu alloy nanoparticle study<sup>[21]</sup>. The overall mass distribution map of  $Pd_{43}Sn_{57}$  nanoparticles is shown in Figure 6(B). During the fuel cell operation, the nanoparticle catalysts exhibited mm-size movement, which leads to accumulation and disappearing in some areas. Meanwhile, the average atomic compositions of the nanoparticle catalyst also showed mm-size fluctuation. The *in-situ* HEXRD/PEMFC experiment is able to capture the dynamic evolution process of electrocatalysts in terms of phase structures as simulated by PDF/RMC analyses. As shown in Figure 6(C), fresh  $Pd_{43}Sn_{57}$  nanoparticles exhibited an orthorhombic-type nanophase structure instead of the conventional fcc phase structure. After about 1 hour operation in the fuel cell,  $Pd_{43}Sn_{57}$  nanoparticles experienced obvious leaching of Sn species and evolved into a mixed phase structure containing 87% hexagonal and 13% fcc nanophases. This nanophase structure segregation remained unchanged after additional 5 more hour's operation but with a different phase type content, i.e., 79% hexago-



**Figure 5** (A) Energetics of O-O bond cleavage in  $O_2$  molecule on fcc and bcc structured PdCu (100) surfaces; (B) Plots of the ORR specific activity and the percentage of fcc structure in the catalyst annealed at different temperatures<sup>[15]</sup>. (color on line)





**Figure 6** (A) Map of the first atomic PDF peak for Pd<sub>43</sub>Sn<sub>57</sub> nanoparticle catalyst in *operando* experiment; (B) Mass distribution of Pd<sub>43</sub>Sn<sub>57</sub> nanoparticle catalyst in the membrane electrode assembly after 70 min operation; (C) Atomic PDFs of Pd<sub>43</sub>Sn<sub>57</sub> nanoparticle catalyst during *in-situ* fuel cell operation<sup>[28]</sup>. (color on line)

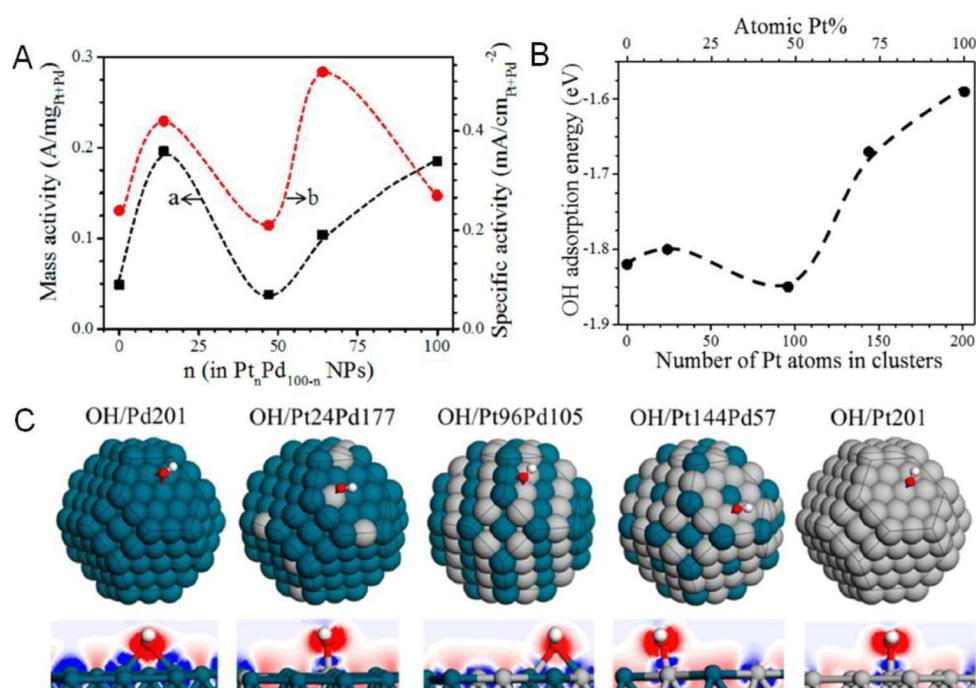
nal and 21% fcc nanophases. The lattice strain largely controlled by the chemical composition was found to be responsible for the initial quick activity decay, while the further particle aggregation drove the following activity decay. The applied electrochemical potential on the catalyst under harsh fuel cell working condition is a strong driving force to induce such phase structure evolution. Similar effect on the phase structure evolution has also been revealed by thermochemical calcination<sup>[8]</sup>.

### 2.3 PdPt

In addition to Pd-based nanoalloys containing non-noble transition metals, noble-metal nanoalloys such as PdPt alloy nanoparticles have also shown intriguing electrocatalytic activities for ORR. Such nanoalloys do not undergo dealloying as in alloys with base metals, and have attracted increasing attention<sup>[29,30]</sup>. PtPd nanoalloy particles with different atomic compositions were studied by Wu et. al. as ORR electrocatalysts<sup>[30]</sup>. As shown in Figure 7(A), the ORR activity is highly dependent on the composition of binary PtPd alloys, showing a maximum ORR mass activity on Pt<sub>14</sub>Pd<sub>86</sub> and a minimum mass activity on Pt<sub>47</sub>Pd<sub>53</sub>. DFT calculations were performed to investigate the composition-activity relationship of PdPt alloys (Figure 7(B), (C)). The strongest adsorption energy of OH was found on Pt<sub>96</sub>Pd<sub>105</sub> cluster model, which correlated well with the experiment result

showing the lowest ORR activity. The combination of experiments and calculations demonstrated that the OH species act as a poisonous intermediate during ORR. The adsorption of reaction intermediates should neither be too strong nor too weak for an optimal reaction kinetics. This aspect is well explained by the Sabatier principle in heterogeneous catalysis. The exploration of optimal adsorption of key intermediates of ORR, e.g., \*O, \*OH, \*OOH, and reasonable reaction kinetics is part of the current investigations, which involve reliable computational screening methods to aid the catalyst design.

The synergistic properties of the dual-noble-metal PdPt system are further exploited by introducing a third non-noble metal into ternary catalysts to enhance the catalytic performance toward ORR. One PdPtCu nanoparticle ORR electrocatalyst has been recently reported by Wu et. al.<sup>[21]</sup>. Engineering the lattice strain of catalysts by composition manipulations incubates a highly active and durable ORR catalyst. The high activity and stability are attributed to an alloying-dealloying-realloying process, in which the structure of nanoparticle catalyst dynamically evolves to a thermodynamically-stable state. Pd plays a crucial role in the alloy catalyst to enhancing the catalytic performance via introducing the synergistic effect on the activity and stability. As demonstrated by the DFT calculations, the participation of Cu in the catalyst



**Figure 7** (A) Plots of the mass activity and specific activity as a function of chemical composition in PtPd/C alloy catalysts; (B) Variation of OH adsorption energy based on PtPd cluster model with composition; (C) The most stable adsorption configurations of OH on different PtPd alloy cluster models<sup>[30]</sup>. (color on line)

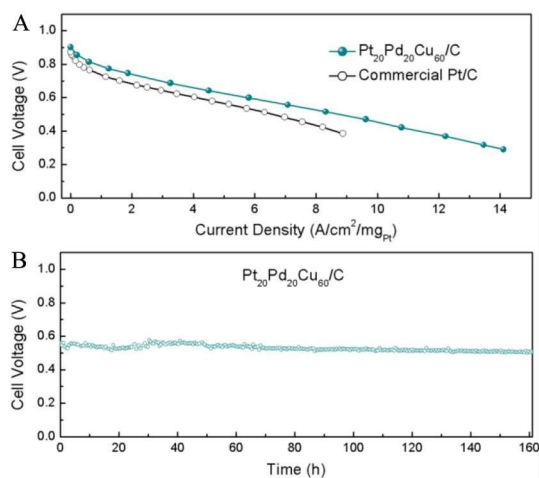
greatly reduces the activation barriers for some key elementary steps during the ORR, boosting the reaction energetics. In contrast to many of the highly active ORR electrocatalysts which perform poorly in the practical fuel cell, the PdPtCu ternary catalyst is shown to exhibit high activity and stability. This is

demonstrated by the performance test of the catalysts in a PEMFC device (Figure 8), showing potential for promising applications in PEMFCs.

It is evident that the understanding of detailed phase structure and dynamic structural evolution under reaction conditions is important for assessing composition-structure-activity relationships of Pd-based nanoparticle, especially nanoalloy electrocatalysts for ORR. *In-situ/operando* HE-XRD characterizations is shown to be powerful to aid the understanding<sup>[8, 18]</sup>.

### 3 Ethanol Oxidation Reaction

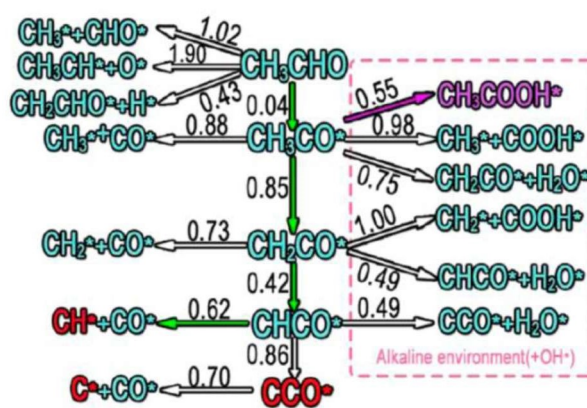
Unlike ORR, EOR involves multiple bond cleavages, i.e., breaking C-H and C-C bonds, which could lead to not only multiple intermediates, but also multiple products depending on the actual bond cleavage. As such, the understanding of the surface species and reaction products in correlation with the surface sites of the catalysts is critical for achieving the most desired product, i.e., the complete oxidation of ethanol to CO<sub>2</sub> (in acidic media) or CO<sub>3</sub><sup>2-</sup> (in alkaline media).



**Figure 8** (A) PEMFC performance curves using PdPtCu and commercial Pt catalysts; (B) Fuel cell stability of PdPtCu catalyst.

### 3.1 EOR Mechanism on Pd

While Pd and Pd-based catalysts are catalytically inert for EOR in an acidic solution, they have been demonstrated to exhibit excellent catalytic performance for EOR in alkaline media which even outperforms that of Pt-based counterparts<sup>[5, 31-33]</sup>. However, the reaction mechanism involving the reaction pathway and the role of some key intermediates of EOR on Pd catalyst remains elusive. As such, Pd (100) surface model was selected to study the reaction pathway of EOR using DFT calculations<sup>[2]</sup>. Adsorbed ethanol molecule firstly prefers to dehydrogenate to form  $\text{CH}_3\text{CHO}$  rather than other C2 (i.e., species containing two carbon atoms) intermediates. The as-formed  $\text{CH}_3\text{CHO}$  is highly active on Pd (100) surface, showing negligible reaction barrier energy to further dehydrogenate to  $\text{CH}_3\text{CO}$  (Figure 9).  $\text{CH}_3\text{CO}$  has been proven to be an abundant intermediate during the EOR process by both experimental methods<sup>[32, 34]</sup> and DFT calculations on Cu (100), Pt (111), Pd (111), and Pd (100) surfaces,<sup>[3, 35, 36]</sup> etc. In alkaline media,  $\text{CH}_3\text{CO}$  is very likely to be coupled by adsorbed hydroxyl group to form acetic acid, which quickly turns to acetate in an alkaline solution<sup>[3, 14, 16]</sup>. This phenomenon was validated by DFT calculations on Pd (100) surface by showing a much lower reaction barrier to form acetic acid comparing with C-H or C-C bond cleavage reactions (Figure 9). The effect of the electrochemical potential on the elementary steps did not change the reaction pathway. The reaction barrier of C-C bond cleavage in  $\text{CH}_3\text{COOH}$  molecule is very high. The formation of acetic acid leads to the partial oxidation of ethanol with only 4 electrons being released rather than the 12-electron complete oxidation pathway, which greatly deteriorates the performance of DEFCs. This finding agrees well with some recent insights on ethanol oxidation. The formation of acetic acid and the high barrier in cleaving C-C bond are two major issues of current investigations toward achieving efficient EOR electrocatalysts<sup>[2, 3, 10, 14, 16]</sup>. Alloying Pd with other metals and designing unique structures might change the reaction pathway to achieve complete oxidation, which has been demon-

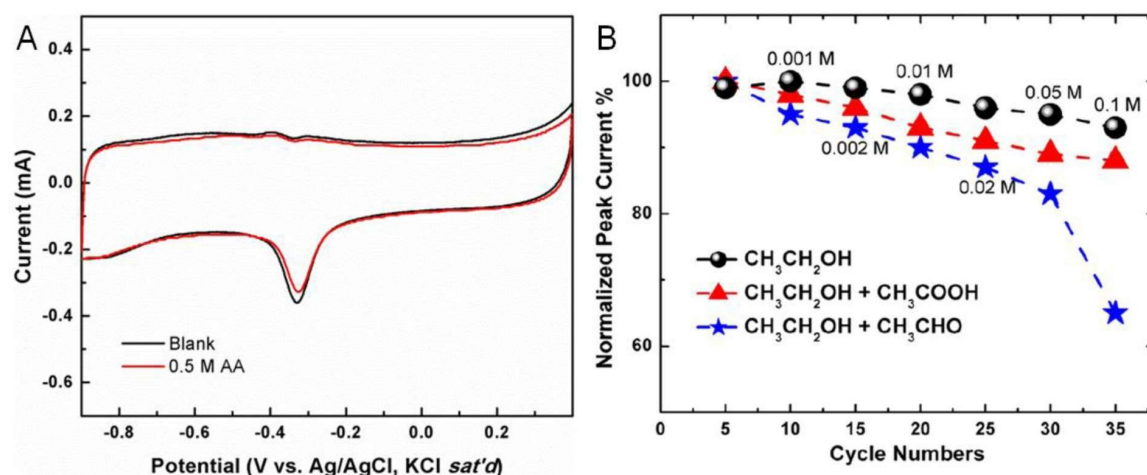


**Figure 9** The partial reaction network showing the reaction barriers of each elementary step during ethanol oxidation on Pd (100) surface<sup>[2]</sup>. (color on line)

strated by some recent works<sup>[10]</sup> and also serves as important research topics for future works.

To aid the understanding of the mechanistic EOR pathways, electrochemical examinations on some of key intermediates, e.g.,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$ , were carried out. As shown in Figure 10(A), the addition of acetic acid in the system using carbon-supported Pd (Pd/C) nanoparticle electrocatalyst didn't give any additional redox peak, especially for the oxidation of acetic acid, which demonstrated that Pd/C electrocatalyst could barely further oxidize acetic acid. This agrees well with the aforementioned theoretical calculation results. On Pd (100) surface, ethanol preferred to be partially oxidized to acetic acid, which is a poisonous species and is very hard to be further oxidized. As shown in Figure 10(B), two key ethanol oxidation intermediates, i.e.,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$ , were gradually injected into the EOR system. The presence of  $\text{CH}_3\text{COOH}$  during EOR slightly depressed the current density. This is consistent with the above results, where acetic acid can deactivate the catalyst by adsorbing on the surface and hence blocking the active sites. For comparison, the addition of  $\text{CH}_3\text{CHO}$  in the EOR system gave even lower current outputs and the color of the solution in the cell turned to be yellow, indicating that the aldol condensation reaction might happen to form dimers which deactivated the catalyst. The detection of inter-





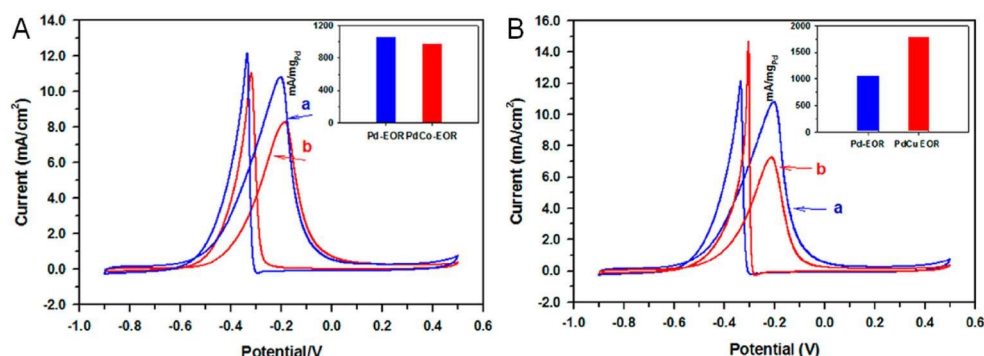
**Figure 10** (A) Cyclic voltammetric curves of Pd/C catalyst in pure 0.5 mol·L<sup>-1</sup> KOH solution (blank) and in 0.5 mol·L<sup>-1</sup> KOH solution with the addition of 0.5 mol·L<sup>-1</sup> acetic acid (0.5 mol·L<sup>-1</sup> AA); (B) Normalized peak current on the forward sweep of EOR on Pd/C catalyst in 0.5 mol·L<sup>-1</sup> KOH solution with increasing concentrations of pure ethanol, ethanol with acetic acid, and ethanol with acetaldehyde<sup>[2]</sup>. (color on line)

mediates during EOR is very crucial to understand the reaction mechanism and to aid the catalyst design, which could be realized by combining advanced *in-situ* mass spectroscopic experiments and DFT calculations.

### 3.2 PdCo and PdCu

Another study evaluated the electrocatalytic performance for ethanol oxidation on PdCo, PdCu, and Pd nanoparticle electrocatalysts<sup>[37]</sup>. As shown in Figure 11, in comparison with monometallic Pd, binary Pd-Co catalyst showed a similar, but PdCu catalyst exhibited a much better EOR mass activity in an alkaline electrolyte. The difference in electrocatalytic performance can be explained by the surface Pd atom

enrichment of PdCu alloy in contrast to the surface Co atom enrichment of PdCo alloy nanoparticles. The differences in surface energy and oxophilicity between base metals (Cu and Co) and noble metal Pd played a crucial role in the electrocatalytic reactions. Comparing with PdCo alloy, the addition of Cu in Pd-based alloys resulted in a more positive shift in the reduction potential of surface oxygenated Pd species. The surface structure engineering of nanomaterials is crucial to understanding the reaction mechanism and preparing the catalysts by design. Given the findings in this work, further studies will seek gaining an in-depth insight into the catalytic synergy of the multimetallic alloy or core-shell nanocatalysts



**Figure 11** Cyclic voltammetric curves for different catalysts in 0.5 mol·L<sup>-1</sup> KOH solution containing 0.5 mol·L<sup>-1</sup> ethanol. (A) Pd/C (a) and PdCo/C (b); (B) Pd/C (a) and PdCu/C (b). Inserts are the corresponding comparisons of mass activities<sup>[37]</sup>. (color on line)

with the aid of computational modeling.

### 3.3 PdAu

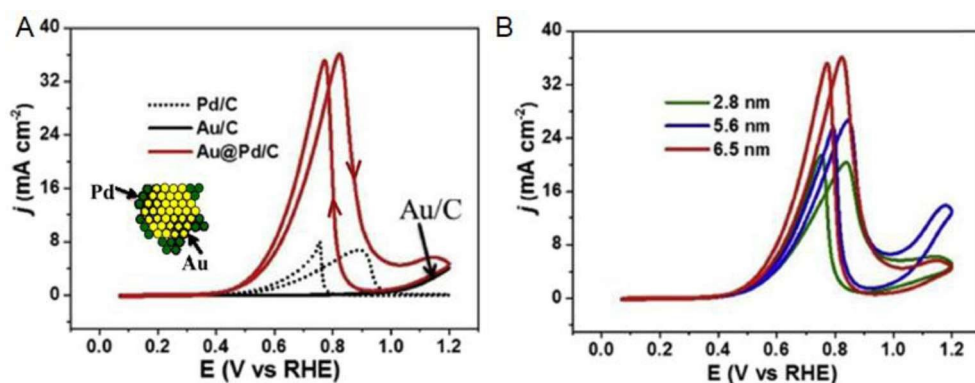
In addition to alloying Pd with different transition metals, the rational core-shell structural arrangement of Pd with different transition metals is also an important pathway for the design of EOR nanocatalysts towards achieving the desired catalytic activity. Indeed, core-shell structure nanocatalysts are gaining increasing research attention due to the unique properties enabled by the well-designed geometric and electronic structures at the atomic level<sup>[8]</sup>. Au nanoparticles in different particle sizes were partially coated by Pd shells, forming Au@Pd core-shell electrocatalysts with surface AuPd alloy exposure<sup>[33]</sup>. The Au@Pd core-shell electrocatalysts greatly outperformed Pd and Au nanoparticles by showing a much higher forward peak current density and a more negative onset potential (Figure 12(A)). An investigation of the Au core size on the catalytic activity revealed that the growing Au core size boosted the corresponding EOR activity via both strain and ligand effects from the Au core (Figure 12(B)). The bifunctional reaction mechanism in the AuPd system needs further investigations using DFT calculations. Beyond Pd-based nanomaterials, Pt-based nanocatalysts were also applied as alcohol oxidation electrocatalysts<sup>[38, 39]</sup>. The structure-activity correlation revealed a strong dependence of the catalytic performance on the initial composition and surface element enrichment of nanomaterials. *In-situ* experiments are expected to provide additional insights into the dynamic structure evolution and

the reaction mechanism for a better design of efficient EOR catalysts.

These selected examples demonstrate that EOR reaction pathways and intermediates or products are strongly dependent on the surface sites and phase structures of the Pd and Pd alloy or core-shell structured catalysts. Rational alloying or core-shell structuring of the Pd nanoparticles with different transition metals enables fine tuning of the catalytic properties.

## 4 Summary

In summary, recent studies of electrocatalysts by combining experimental and theoretical approaches have provided some fresh insights into the important role of the nanophase structures, alloy compositions, and key intermediates in electrocatalytic ORR and EOR over Pd and Pd-based nanomaterials. The design of efficient electrocatalysts for ORR and EOR in fuel cell reactions depends heavily on the fundamental understanding in the nanophase structures of the nanocatalysts and the reaction mechanisms in terms of reaction intermediates. This understanding is aided by *in-situ/operando* HE-XRD/PDF characterization and DFT computation, leading to fundamental insights into the dynamic nature of the nanocatalysts in fuel cell reactions. Further in-depth *in-situ/operando* measurements by coupling nanocrystal structure analysis techniques with surface-sensitive techniques, as well as theoretical modeling and calculations, are part of our investigations aiming at demonstrating the commercialization viability of the nanocatalysts in



**Figure 12** Cyclic voltammetric curves for different catalysts in 1.0 mol·L<sup>-1</sup> NaOH solution with 1.0 mol·L<sup>-1</sup> ethanol. (A) Au/C, Pd/C, and Au@Pd/C; (B) Au@Pd/C catalysts with varying Au core particle sizes<sup>[33]</sup>. (color on line)

fuel cells.

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## 钯基氧还原和乙醇氧化反应电催化剂： 关于结构和机理研究的一些近期见解

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**摘要:** 质子交换膜燃料电池和直接乙醇燃料电池已成为可持续性清洁能源研究的一个聚焦点。在燃料电池中, 氧还原反应和乙醇氧化反应是两个重要的反应, 其相关高活性、高稳定性并且廉价的催化剂的研发仍然存在很多问题, 极大地制约了燃料电池的大规模商业化应用。其中的挑战主要来自于对纳米催化剂结构和反应机理的有限认识。由于实验表征理论计算的结合, 对钯基金属纳米材料电催化剂的研究得到了很大的进展。本文从实验和理论计算两个方面出发, 重点讨论了应用于氧还原反应和乙醇氧化反应的钯和钯基电催化剂的结构和反应机理方面的近期研究的一些见解。这些见解对未来催化剂的设计与优化有一定的启发意义。

**关键词:** 氧还原反应; 乙醇氧化反应; 电催化剂; 相态结构; 反应机理; 燃料电池