Tuning Electrocatalytic Activity of Pt Monolayer Shell by Bimetallic Ir-M (M = Fe, Co, Ni or Cu) Cores for the Oxygen Reduction Reaction

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Abstract

Platinum monolayer electrocatalyst are known to exhibit excellent oxygen reduction reaction (ORR) activity depending on the type of substrate used. Here we demonstrate a relationship between the ORR electrocatalytic activity and the surface electronic structure of Pt monolayer shell induced by various IrM bimetallic cores (M = Fe, Co, Ni or Cu). The relationship is rationalized by comparing density functional theory calculations and experimental results. For an efficient Pt monolayer electrocatalyst, the core should induce sufficient contraction to the Pt shell leading to a downshift of the d-band center with respect to the Fermi level. Depending on the structure of the IrM, relative to that of pure Ir, this interaction not only alters the electronic and geometric structure but also induces segregation effects. Combined these effects significantly enhance the ORR activities of the Pt monolayer shell on bimetallic Ir cores electrocatalysts.

Keywords

Fuel Cells; Electrocatalysis; Density function theory; Core-shell catalyst; Pt monolayer; Oxygen reduction reaction

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Graphical Abstract

Introduction

The quest for efficient electrocatalysts overcoming the drawbacks like inadequate efficiency of energy conversion, cost and durability remains a challenging and ultimate goal for fuel cell research [1, 2]. As the proton exchange membrane fuel cells (PEMFC) cathode is exposed to high operating potential and acidic environment most transition metal dissolves, reducing its efficiency. So numerous studies linking to increase the ORR activity by alloying Pt with another transition metal has gained momentum [3, 4]. These include core-shell structured nanoparticles [5-7], de-alloyed [8-10] and porous structured nanoparticles [11] and structurally ordered intermetallics [3, 12]. A leap forward to attain the goal of reducing the Pt loading and simultaneously enhancing the ORR activity and stability was attained by depositing a Pt monolayer (Pt_{ML}) on a Pt-free substrate [13, 14]. Our group has been focusing on the design and synthesis of core-shell structure catalysts and has developed a class of catalysts consisting of a Pt_{ML} on different substrate metals and alloys. In addition, by properly selecting the metal core, the activity of the Pt_{ML} shell can be heightened through electronic and/or geometric effects [15, 16]. It is well known that the degradation of transition metal cores in the core-shell catalysts is the major problem under harsh fuel-cell operation conditions. Our previous work on a relatively stable transition metal like Pd also undergoes certain dissolution from the cores in Pd@Pt core-shell catalysts [17]. One of the difficulties in determining the effect of the core in using Pt monolayer catalysts is that the activity of the catalyst can have a wide range of values depending on its microstructure and/or method of preparation [18, 19].

Iridium is one of the most stable metals [20] and its activity towards the ORR with Pt_{ML} is only slightly enhanced. Density functional theory (DFT) calculations for single crystals of Ir show that the Pt_{ML} on Ir (111) surfaces causes too strong contraction in Pt–Pt bonding and the

binding energy of oxygen to Pt becomes too small, in agreement with the experiment [16, 21]. Theoretically, extensive attempts have been carried out to understand the Pt_{ML} ORR kinetics using DFT calculations, which provide substantial insights into the ORR [16, 17]. Recently, IrM (M = Ni, Cu, Fe) substrates for the Pt_{ML} shell have shown a good activity and stability [16, 22, 23] but their electrocatalytic trends with respect to surface electronic structure and segregation effects are not well explored [24]. Here we emphasize on the concepts that can be used to understand variations in the ORR activity caused by the effects of various IrM bimetallic cores on the Pt monolayer electrocatalyst. We focus on the electronic structure modification of the IrM bimetallic core substrate to identify the more active and stable Pt_{ML} nanocatalysts. Using bimetallic Ir cores facilitates tuning of the properties of a Pt shell. The results suggest that apart from their surface geometries and electronic modifications, surface segregation effects signify changes in catalytic behavior in regard to alloying of various transition metals with Ir.

Experimental

Material synthesis

The carbon supported iridium-metal bimetallic catalysts were prepared by mixing and simultaneously sonicating an equal molar ratio of (NH₄)₂IrCl₆ with Ni(HCO₂)₂·2H₂O or FeCl₂·4H₂O or CuSO₄·5H₂O or Co(NO₃)₂·6H₂O salts with high-area Vulcan XC72R carbon black in Millipore water to obtain 20 wt.% total metal. After an hour of sonication, NaBH₄ solution was added to reduce the precursors with continued ultrasonication for an hour. The as-obtained carbon-supported IrM nanoparticles were rinsed with water and dried in vacuum overnight. The dried samples were subjected to an annealing process at 600°C in 15 % H₂/Ar for 2 h.

Electrochemical Measurement

Catalyst inks of carbon-supported IrNi, IrFe, IrCu, IrCo nanoparticles were prepared by mixing 5 mg of catalysts with 5 mL of 18 M Ω water. The solution was sonicated until a dark, uniform ink was achieved. Rotating disc electrodes (RDE) of the nanoparticles were prepared by placing 10 μ l of nanoparticle suspension onto a flat glassy carbon electrode (5 mm diameter, Pine Instrument). After drying in vacuum, the electrodes were covered with 10 μ l of a dilute Nafion solution (2 μ g/5 μ l) and dried again. The Pt monolayer was placed on each of the RDE electrodes by galvanic displacement by Pt of a Cu monolayer formed by under-potential deposition (UPD). The Cu monolayer was deposited in a 50 mM H₂SO₄ + 50 mM CuSO₄ solution. The electrode covered with a Cu monolayer, was immersed in a 1.0 mM K₂PtCl₄ + 50 mM H₂SO₄ solution to displace the Cu with Pt. The Pt content in the RDE samples was derived from the Cu UPD charge. A leak-free reference electrode (Ag/AgCl) was used and all the potentials are given with respect to a reversible hydrogen electrode (RHE). A platinum wire served as the counter electrode. The electrolytes were prepared from Optima sulfuric acid and perchloric acid (Fisher), and Millipore water. Electrochemical studies were conducted in a three-electrode glass cell using a CHI 700B electrochemical analyzer or PGZ402 Volta-Lab potentiostat. All electrochemical measurements were performed in 0.1 M HClO₄ solution. Polarization curve for the ORR was obtained in O₂-saturated solution by scanning the potential from 0 to 1.1V versus RHE (scan rate: 10 mV s⁻¹; rotation rate: 400, 625, 900, 1225, 1600 and 2025 rpm). For calculating the activity of the catalysts, the kinetic currents for ORR were determined using the Koutecky-Levich equation [19, 25].

Characterizations

X-ray diffraction (XRD) analyzes of the IrM nanoparticles were carried out using a Phillips 3100 diffractometer equipped with a CuK α source (1.54056 Å). The diffraction patterns were collected from 30° to 80° at a scanning rate of 0.4° per minute, with a step size of 0.02°. Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL) was used for Scanning transmission electron microscopy and Electron Energy Loss Spectroscopy (STEM-EELS) analysis. The microscope is equipped with a cold field emission electron source and a high resolution Gatan Enfina energy-loss spectrometer. For this study, we performed STEM imaging and EELS using a 1.3 Å electron probe with a probe current ~50 pA. The STEM convergence angle is around 28 mrad while the collection angle is from 114 to 608 mrad. In this experimental condition, the contrast of images directly related with atomic number (Z-contrast). The energy resolution for EELS is about 0.4 eV estimated from the half-width of zero loss peaks. The carbon-supported nanoparticles were dispersed in water and then deposited on a lacy-carbon TEM grid (EMS, Hatfield, PA).

DFT calculations

Plane-wave-based density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) code [26, 27]. Similar to the previous studies [16, 28], the projector augmented wave method (PAW) [29] with the generalized gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof (RPBE) functional [30] was applied. Spin-polarized DFT calculations were employed on sphere-like nanoparticle models to simulate the

bimetallic structures of the nanoparticles studied in our experiments, wherein all atoms were allowed to relax fully. The binding energy of atomic oxygen on the (111) plane of a nanoparticle (BE–O) was calculated, and considered as a descriptor for scaling the ORR activity. Our previous studies showed that DFT calculated BE–O based on the hemisphere-like model was able to well describe the experimentally measured ORR activity of core-shell nanoparticles [15, 16]. Here, BE–O is defined as $BE-O = E[O-NP] - E[NP] - E[O]$, where $E[O-NP]$, $E[NP]$, and $E[O]$ respectively, are the calculated electronic energies of an adsorbed oxygen-atom on a nanoparticle, a clean nanoparticle, and a triplet oxygen atom.

Results and discussion

Experimental analysis of the nanoparticles

As per phase diagrams, Ir is known to form solid-solution alloys with Ni, Fe, Co and Cu [31]. Here we used the same synthesizing technique as reported in detail elsewhere [22, 32], and found that even if Ir forms solid solutions when alloyed with Ni, Fe, Co and Cu they vary in their structural architecture. As reported earlier IrNi [32], and IrFe [22] forms a core-shell structure whereas IrCo and IrCu [23] forms a random alloy. We used electrochemical and powder XRD methods to compare and contrast the core-shell and alloy nanoparticles to illustrate how the same synthesizing techniques can differentiate the two types of architectures. Further, we use DFT calculations to establish a relationship in ORR electrocatalytic activity and the surface electronic structure on Pt_{ML} shell caused by various IrM bimetallic cores.

Powder XRD measurements shown in Fig. 1 reveal insights into the structural transformation of IrM nanoparticles. The reflection peak of (111) plane for pure Ir is at 2θ angle of 40.66° (Fig. 1c), but the IrNi and IrFe (111) peaks lie at much higher angles of around 42.65° and 42.05°

respectively indicating their high degree of alloying. The (111) peaks for IrCo and IrCu nanoparticles are at much lower angles (41.3°) (Fig. 1c) revealing a different morphology compared to IrNi and IrFe nanoparticles. Further analysis of the IrCo and IrCu XRD peaks as shown in Fig. 1b indicates small Cu and Co peaks between 2θ angles of 43.5° and 44° revealing their presence on the near-surface of the nanoparticle. These peaks disappeared after acid wash since Cu and Co precipitates were dissolved away [23]. XRD peaks moving into higher angles indicate higher lattice contraction that can be caused due to Ni or Fe atoms diffusing into Ir lattice forming core-shell structures. This indicates that alloying with Ni or Fe, the lattice contraction of the nanoparticles was around 3% higher than the alloying with Cu or Co. It is known that Ir forms a solid solution with these metals, but powder XRD can reveal the high degree of alloy and at the same time put some key insights into their structure. From the (111) XRD diffraction profiles in Fig. 1, the changes in lattice constant (a) relative to bulk Ir (a_{Ir}) can be estimated according to $(a - a_{\text{Ir}})/a_{\text{Ir}}$ and these were -1.6, -1.7, -3.1, and -4.4% for IrCu/C, IrCo/C, IrFe/C, and IrNi/C, respectively. The lattice parameters for the catalysts are smaller than that of pure Ir, and so they are compressively strained. Higher compressive strain is observed on the core-shell structured nanoparticles than the random alloyed nanoparticles. Fig. 2 shows the ORR specific activities from the IrM nanoparticles (Fig. 4c) plotted as a function of the relative lattice strains. Clearly the specific activities increase with an increase in the lattice strains. Though the strains induced by alloying IrM do not show much correlation with the surface strain on Pt_{ML} shell as shown in the DFT calculations below, they can be useful to understand the anti-segregation effects of the nanoparticles. DFT studies have shown that it is energetically more costly to pull out Ir from the $\text{Pt}_{\text{ML}}\text{Ir}$ core and move it to the shell than it is when Ir is in the $\text{Pt}_{\text{ML}}\text{IrNi}$ core favoring the anti-segregation of Ir to the Pt_{ML} shell on interaction

with oxygen [16, 22, 23]. The high compressive strain induced by the Ni core in the IrNi nanoparticles may be the reason for this anti-segregation effect. The Ir-Ir distance calculated from the XRD profiles increases in the order of IrNi < IrFe < IrCo < IrCu, indicating that the core-shell structures favor the anti-segregation of Ir to the Pt monolayer shell.

Core-shell and alloy structures can also be easily identified by STEM-EELS analysis. To represent the core-shell structure we chose IrNi nanoparticles whereas IrCu nanoparticles for the alloyed structure. Figs. 3a and 3d depict low magnification HAADF-STEM images from the IrNi and IrCu samples respectively. Most of particles are round and have sphere-like shapes that are well dispersed on the carbon substrate. The Z contrast images from the IrNi HAADF image show bright Ir shells on relatively darker Ni cores (Fig. 3a), signifying the formation of a core-shell structure. These distinct characteristics were missing in the IrCu HAADF images (Fig. 3d) indicating the formation of random alloys. Figs. 3c and 3b show the representative single nanoparticle and its corresponding signal intensity profiles of Ir and Ni components respectively, in a line scan across the whole nanoparticle (arrow). The EELS line-scan profiles of Ni and Ir from the single nanoparticle reveal the core-shell structure of the nanoparticle with Ni in the core covered by Ir shell. Whereas, similar line-scan profiles of Ir and Cu from a single IrCu nanoparticle indicate a homogeneous alloyed structure (Figs. 3e&f).

To investigate the influence of different cores on the Pt_{ML}, Pt_{ML} catalysts were prepared via galvanic replacement of platinum on under-potential deposition of Cu monolayer. Cyclic voltammograms (CVs) recorded in an Ar-saturated 0.1 M HClO₄ solution (Fig. 4a), reveal that the hydrogen adsorption/desorption (Hupd) and oxide species adsorption/desorption regions resemble those of Pt/C surface. ORR polarization curves of the Pt_{ML} on IrM nanoparticles in an electrolyte consisting of 0.1 M HClO₄ purged with O₂ is shown in Fig. 4b. The IrNi and IrFe

nanoparticles with core-shell structures have almost twice the ORR activity than the IrCu and IrCo nanoparticles with random alloy structures. The Pt mass activities along with their specific activities as shown in Fig. 4c clearly demonstrate that core-shell structured nanoparticles are the most preferred substrates for the Pt_{ML} electrocatalyst. Moreover it has been shown that the core-shell-structured IrNi and IrFe retain their structural morphology after the harsh potential cycling [16] while IrCu suffers chemical leaching of Cu under the same conditions [23]. Thus the roles of its substrate components and configurations on the activity and stability differ in the Pt_{ML} catalysts.

Theoretical analysis of Pt_{ML} IrM nanoparticles

Similar to our previous study on Pt_{ML}IrNi nanoparticles [16], we performed DFT calculations to understand the correlation of Pt_{ML}IrM and the ORR activities. We constructed sphere-like nanoparticles of ~1.7 nm based on a truncated octahedron model as shown in Fig. 5a. In the surface segregation study, we used the method described in the previous work where the segregating atom switches positions with one atom of the surface layer (PtIr_{1,ML}IrNi in Figs. 5c and 5d). The DFT study on Pt_{ML}IrNi demonstrated that the anti-segregation effect under the ORR condition supports experimental findings. Here we used the same technique for Pt_{ML}IrFe since the STEM/EELS results clearly show that IrFe has the core-shell structure [22]. However, we did not take into account the anti-segregation effect on Pt_{ML}IrCu and Pt_{ML}IrCo due to their randomly mixed character [23]. Moreover it has been shown that due to the presence of Co atoms on the surface of the IrCo alloy, Co tend to segregate to the surface under ORR conditions suppressing its activity [33, 34]. We calculated the BE–O that serves as a descriptor for scaling the ORR activity [16]. Fig. 5b shows that partially replacing M in the core weakens the BEO,

and introduces more contraction therein ($\text{Pt}_{\text{ML}}\text{IrNi}$: 3.45 eV and 4.12%, $\text{Pt}_{\text{ML}}\text{IrFe}$: 3.55 eV and 3.96%, $\text{Pt}_{\text{ML}}\text{IrCu}$: 3.46 eV and 3.99%, and $\text{Pt}_{\text{ML}}\text{IrCo}$: 3.44 eV and 4.08%) compared to that of Pt (4.10 eV and 3.04%). Fig. 5c plots the BEO variation against the d-band center compared to the Pt nanoparticle, which exhibits a strong correlation and shifts the d-band center of Pt in the shell away from the Fermi level by the IrM core, thereby lowering the BEO. We note that in this study we used the averaged d-band center and BEO of $\text{Pt}_{\text{ML}}\text{IrFe}$ without and with the anti-segregation effect ($\text{PtIr}_{0.5,\text{ML}}\text{IrFe}$) to obtain a better correlation (−2.16 eV and −3.69 eV, respectively). Fig. 5d illustrates the calculated BEOs versus the measured ORR specific activities for Pt/C and $\text{Pt}_{\text{ML}}\text{IrM/C}$. As described, the BEOs for $\text{Pt}_{\text{ML}}\text{IrNi}$ and $\text{Pt}_{\text{ML}}\text{IrFe}$ correspond to the strength of O binding after the exchange of Ir in the core with Pt in the shell ($\text{PtIr}_{1,\text{ML}}\text{IrNi}$ and $\text{PtIr}_{0.5,\text{ML}}\text{IrFe}$). The volcano-like plot manifests that $\text{Pt}_{\text{ML}}\text{IrCo}$ and $\text{Pt}_{\text{ML}}\text{IrCu}$ bind O too weakly to dissociate oxygen, whereas Pt nanoparticles does O too strongly to be removed from the catalyst. Overall, the DFT simulation demonstrates that the geometric, electronic, and segregation effects under fuel cell conditions have a key role in rationalizing the increase in the ORR activity of $\text{Pt}_{\text{ML}}\text{IrM/C}$.

Conclusions

IrM nanoparticles synthesized using similar techniques can differentiate into two types of architectures. IrNi and IrFe form core-shell structures while IrCo and IrCu form random alloys. Core-shell structures and random alloyed IrM nanoparticles depending on their electronic, geometric and segregation effects compared to pure Ir, enable widely different ORR activities for the Pt_{ML} electrocatalyst. Experimental studies show that IrM core-shell structured nanoparticles induce the higher lattice strain and serve as a better substrate for the Pt_{ML} electrocatalyst. The

results suggest that coupling DFT studies with experimental results has a distinct merit, signifying changes in catalytic behavior in regard to the structure-function relationship of various transition metals with iridium.

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Figure legends

Figure 1. (a) Powder XRD for IrNi and IrFe core-shell samples. (b) Powder XRD for IrCu and IrCo alloy samples. (c) XRD enlarged region of the IrM samples taken from (a) and (b).

Figure 2. ORR specific activities for Pt_{ML} IrNi/C, Pt_{ML} IrFe/C, Pt_{ML} IrCu/C, Pt_{ML} IrCo/C, and Pt_{ML} Ir/C at 0.9 V plotted as a function of IrM lattice strain determined by the XRD patterns.

Figure 3. (a, d) Low magnification HAADF-STEM images of IrNi core-shell nanoparticles and IrCu alloy nanoparticles respectively. HAADF-STEM images of a single nanoparticle from (c) IrNi and (f) IrCu and their corresponding EELS line-scan profiles (b, e) along the line as shown in their respective HAADF images.

Figure 4. (a) CVs of Pt_{ML} IrM/C nanoparticles in an Ar-saturated 0.1 M HClO₄ solution (scan rate = 20 mV/s). (b) Comparison of ORR polarization curves for Pt_{ML} IrM/C nanoparticles at 1600 rpm in O₂-saturated 0.1 M HClO₄ (scan rate = 10 mV s⁻¹). (c) Comparison of Pt mass and specific activities at 0.9 V.

Figure 5. DFT modeling (a) schematic of a Pt_{ML}IrM model (M=Ni, Fe, Cu, Or Co). Binding energy of oxygen (BEO) of Pt and Pt_{ML}IrM nanoparticles against, (b) surface strain, (c) d-band center, and (d) specific activities of Pt/C and Pt_{ML}IrM/C.

Bio-sketch

<p>Dr. Kurian Kuttiyiel is an associate research scientist in the Department of Chemical Engineering at Columbia University. He received his Ph.D. in Material Science and Engineering from Stony Brook University in 2011. Apart from electrochemical and synchrotron-based characterization of materials, his research interests include synthesis of nanostructured materials for energy conversion which include core-shell structured nanoparticles and structurally ordered intermetallic nanoparticles.</p>
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Dr. Radoslav Adzic is a senior chemist at the Brookhaven National Laboratory. He graduated from the University of Belgrade in 1974 with a Ph.D. in chemistry. He is a Fellow of the Electrochemical Society and of International Society of Electrochemistry and correspondent member of the Serbian Academy of Arts and Sciences. He has more than 300 scientific publications in the field of electrochemistry and 20 U.S. patents. He has won numerous awards, including the SciAm 50 Award in 2007 and the U.S. Department of Energy's Hydrogen R&D Award in 2008 and in 2012. Lately his group won the "R&D 100" for Pt Monolayer catalyst.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Graphical Abstract