

Short communication

Combinatorial screening and nano-synthesis of platinum binary alloys for oxygen electroreduction

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Abstract

The catalytic oxygen electroreduction properties of platinum alloyed with base metals were screened using a high throughput combinatorial method. Candidate catalysts were identified by comparing the activity–stability–composition relationships between the platinum alloys and a pure platinum standard. Among the alloys studied, PtCo, PtNi, PtZn, and PtCu displayed the highest catalytic activities towards molecular oxygen electroreduction, but suffered from poor chemical stability in acid electrolytes. Alloys based on PtW, PtTi, and PtSe offered modest catalytic activity improvements and good chemical stabilities. In addition to the high throughput discovery, various synthesis technologies were studied to engineer alloy particles on the nanoscale. A good correlation in catalytic activity was found between thin film and carefully engineered powder catalysts.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are a promising candidate as an environmentally friendly power source for transportation applications [1–3]. The advantages of PEMFCs over internal combustion engines (ICEs) are a relatively high efficiency, low or zero emissions, and a high energy density. The high efficiency of PEMFCs arises from the direct conversion of chemical energy to electrical energy without the Carnot limitation that applies to thermal engines. Governments and automobile companies have committed billions of dollars to push fuel cells powered vehicles (FCVs) into mass market because of the potential energy crisis and stringent government pollution regulations. However, three major issues currently inhibit the mass marketing of PEMFCs in transportation, namely, high component costs, a less established refueling infrastructure, and poor durability of the system in service. The cost and durability issues are predominately related to the electrolyte and electrocatalysts used in PEMFCs. To overcome the material barrier of precious metal based electro-

catalysts, new electrocatalysts must be developed with reduced precious metal content while maintaining high catalytic activity. Though considerable efforts have been made over past decades to find new catalysts, particularly Pt alloy electrocatalysts, for molecular oxygen electroreduction [4–11], little attention has been paid to the systematic investigation of the activity–stability–composition relationships of these alloys and no clear candidate catalyst has been found for next generation FCVs.

Combinatorial high throughput research is becoming more and more popular, both academically and industrially, in pharmaceutical, material, and chemical research. A great deal of applied research has been conducted worldwide involving the rapid testing of large numbers of composite materials with the purpose of finding new beneficial materials [12–18]. On one side, the large number of combination does increase the chance of finding desired materials; however, this method can waste resources and time by creating a large amount of useless data. To avoid wasting resources and to produce more reliable data, as in the case of conventional single-experiment measurements, we have developed a novel high throughput method where the number of experiments is smaller than typical industrial combinatorial research, yet providing data as reliable as from conventional single-experiment [19,20].

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In addition to discovering new electrocatalyst materials, synthesis of these materials on the nanoscale is critical to achieve optimized catalytic performance. Nanostructured materials have attracted increasing attention due to displaying unique properties not observed in bulk materials. Important challenges in developing nanostructured materials include the ability to control the size of a nanoparticle, monodispersity, microcomposition, and even the capability for morphology or self-assembly capability, so called nanomaterials by design [21]. Recently, great progresses have been achieved in particle nano-engineering through the development of various synthesis technologies [20,22–27], demonstrating remarkable parallels to catalytic activities for supported nanoparticles.

This paper reports the results of thin film based high throughput combinatorial screening and nano-synthesis of Pt binary alloys for catalytic oxygen electroreduction.

2. Experimental

A high throughput combinatorial method was developed to systematically study the electrocatalytic reduction of molecular oxygen of thin alloy films [19,20]. Thin alloy films of 100 nm in thickness with defined compositions were fabricated in the form of solid solution by a multi-source physical vapor deposition (M-PVD) system. The resulting thin film samples were analyzed for morphology by scanning electron microscopy (SEM), composition by energy dispersive X-ray spectroscopy (EDXS), and phase formation by X-ray diffraction (XRD) prior to electrochemical stability testing and activity screening on a multi-channel rotating disk electrode (M-RDE) system. A final compositional analysis was performed to determine if any composition changes occurred during electrochemical analysis. All data and information were entered into a database for further analysis and visualization.

The M-PVD system is equipped with 12 plasma guns in 3 clusters. Up to four elements can be deposited simultaneously forming solid solutions. The atomic composition of each metal in the alloy (solid solution) was controlled by varying plasma powers and the film thickness was controlled by the plasma power, deposition time, and gas pressure. The physical vapor deposition is an atomistic deposition process, it is a simple and convenient way to make solid solution films comprised of multiple elements. The oxygen reduction properties of thin alloy films were electrochemically screened by the hydrodynamic M-RDE system. The system consists of 16 stations each containing a conventional rotator (working electrode), a glass cell, a counter electrode, and a reference electrode in a typical three compartment cell configuration. Individual glass cells were utilized for each working electrode to protect against cross contamination of base metals that may be leached out from the alloys in acidic electrolytes. By using a multi-channel potentiostat, the reactions on all working electrodes were measured simultaneously. Specially made glassy carbon working electrodes were used as substrates for the thin films. The geometric surface areas of all electrodes were identical, 0.196 cm². The electrolyte used in all experiments was optima grade sulfuric acid diluted with 18 MΩ water to 0.5 M. The electrolyte was deaerated with high purity

argon prior to stability testing (intensive cycling between 0 and 1 V). Saturation with high purity oxygen was performed prior to the electrocatalytic activity screening. The potential was controlled with respect to a saturated calomel reference electrode (SCE) by a Solartron potentiostat. All hydrodynamic polarization measurements were performed under a rotation speed of 2000 rpm and a scan rate of 5 mV s⁻¹.

Carbon supported PtW and PtTi nanoparticles were synthesized through organometallic routines reported elsewhere [28,29]. The powders were characterized by XRD, inductively coupled plasma analysis (ICP), high-resolution transmission electron microscopy (HRTEM), and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). A single channel RDE system from Pine Instruments was used for powder catalytic activity screening. All experimental configuration and approaches were identical to the thin film screening previously mentioned. Samples were prepared by pipetting and uniformly distributing 15 μl of catalyst ink onto 0.196 cm² glassy carbon electrodes. Catalyst inks were prepared by mixing 20 mg of supported catalysts with 20 ml of 18 MΩ water and 1 ml of diluted Nafion solution (5 wt.%, Aldrich). The solution was ultrasonicated using a pulse ultrasonic probe for 10 min or until a dark, uniform ink was achieved.

3. Results and discussion

Catalysts for fuel cells must be active and stable under the thermodynamic forces (temperature, gas atmosphere, pressure, pH, and electrochemical potential) of fuel cell operation. To identify candidate Pt alloys, the following criteria were used. First, Pt mass specific activities were calculated and compared since the reduction of Pt and other precious metals used in the PEMFC cathode is one of the top priorities. To calculate the Pt mass specific activity, Tafel plots were created from hydrodynamic polarization curves using the Levich–Koutecky equation [30,31] and the kinetic current densities (I_K cm⁻², electrode geometric area) were obtained from these plots. The Pt mass specific activity is defined as the kinetic current density normalized by Pt mass. For thin film alloys, the Pt mass-fraction was used instead of Pt mass; therefore, alloy comparisons were made using Pt mass-fraction specific activity. By using the mass (mass-fraction) specific activity, comparison of the catalytic enhancement due to alloying with base metals for a normalized amount of Pt could be made. Fig. 1(a) is a bubble plot displaying the Pt mass-fraction specific activities towards oxygen electroreduction at 0.8 V for 18 Pt binary alloy systems relative to a pure Pt standard. The pure Pt standard was calculated by averaging activities of pure Pt films from all tested libraries. Each bubble represents one alloy from the corresponding alloy system on the X-axis with a Pt atomic concentration indicated on the Y-axis. The size of the bubble is proportional to the relative mass specific activity with larger bubbles indicating higher catalytic activity. For alloys with activities less than that of pure Pt, the bubble size was minimized and held constant to aid comparisons.

Secondly, to avoid being misled by using Pt mass specific activity for ultra low Pt concentration alloys, half-wave potentials (HWP) were used as an additional indicator of activity. The

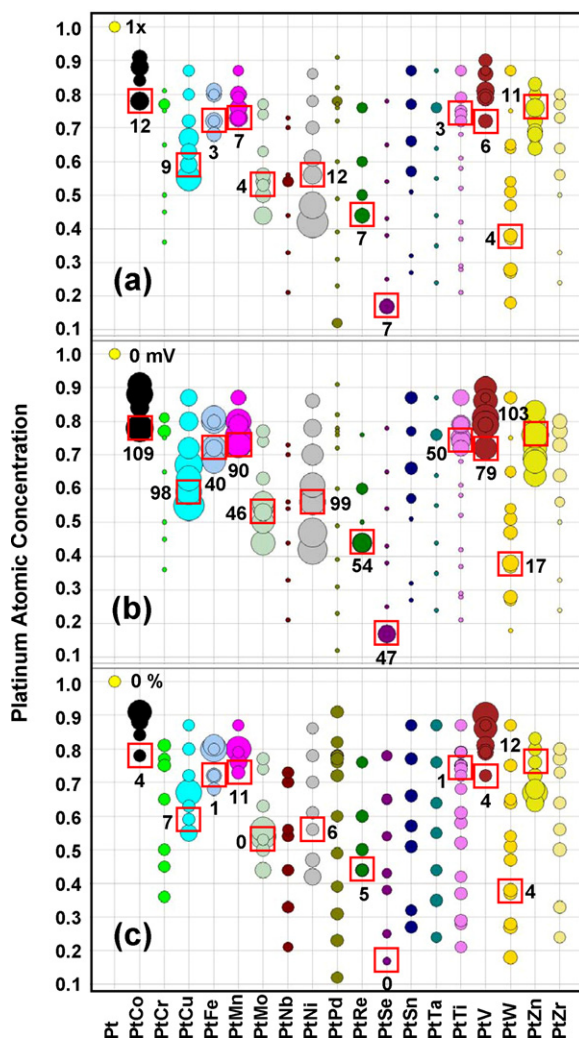


Fig. 1. (a) Relative Pt mass-fraction specific activities at 0.8 V for Pt binary alloys; (b) HWP shifts of these alloys, in comparison with a pure Pt standard; (c) relative changes of Pt atomic concentration of these alloys after electrochemical corrosion testing.

HWP is the potential at half current maximum in the hydrodynamic polarization curve. A positive HWP shift for an alloy catalyst relative to the pure Pt standard indicates the activity of that alloy is better than pure platinum. The activity of alloy catalysts increases with increasing HWP shift. In this way, it is able to avoid sacrificing the fuel cell performance by reducing the platinum mass. Fig. 1(b) shows the HWP shifts of the Pt binary alloy systems. Similar to Fig. 1(a), the size of the bubble is proportional to the magnitude of the positive HWP shift with negative HWP shifts represented by minimized bubbles.

Thirdly, due to the severe operating environment of PEMFCs being characterized by a very acidic electrolyte, a relatively high operating temperature, and an oxidizing atmosphere at the cathode, the chemical and thermal stabilities of electrocatalysts are very important to minimize performance degradation. Therefore, the composition change of the alloys was investigated using EDXS analysis before and after corrosion testing and was included as a comparison criterion. Fig. 1(c) displays the relative changes of platinum atomic concentration of the

alloys as a function of final composition for these alloy systems. The bubble size is inversely proportional to stability, i.e. smaller bubbles indicate less base metal corrosion or a small change in composition after testing. Note that EDXS was used in film compositional analyses and that the error bar of EDXS is typically very high, up to 10–20% for low concentration elements. The stability results are only intended to be used as a qualitative indication of alloy stability. In addition to the composition changes shown in Fig. 1(c), the lack of low Pt atomic concentration alloys in, for instance, PtCo, PtCu, PtFe, PtMn, PtMo, PtNi, PtV, and PtZn alloy systems is another indication of chemical corrosion. The base metals in these highly corrosive alloys were leached away, resulting in compositions with high Pt atomic concentration. Finally, when available, thermodynamic information such as immunity, nobility, and phase formation were also taken into account [32,33].

Candidate alloy catalysts were determined by maximizing Pt mass-fraction specific activity and HWP shift while minimizing alloy corrosivity (composition change). For stable alloy systems, alloys with the highest mass-fraction specific activities and the highest positive HWP shifts are easily identifiable. However, for less stable alloy systems, a compromise in activity was made in order to identify more stable alloys. Using PtCo as an example, an alloy with 78 at.% Pt and 22 at.% Co displayed the largest mass-fraction specific activity and positive HWP shift, and a relatively small composition change after stability testing. Based on the criteria described above, this alloy was identified as the best for the PtCo system. A similar strategy was used to identify the best compositions for other alloy systems. These promising oxygen electroreduction catalyst alloys are framed in Fig. 1. For the sake of quantitative comparison, the relative mass specific activities, HWP shifts, and relative composition changes of these candidate alloys are labeled near the bubbles. Most of the candidate alloy compositions display ratios of Pt to base metal of either 3:1 (PtCo, PtFe, PtMn, PtTi, PtV, and PtZn) or 1:1 (PtCu, PtMo, PtNi, and PtRe), corresponding to the two ordered structures of FCC alloys. The only exceptions are PtSe and PtW, where the catalyst candidates have much lower Pt atomic concentrations. Among the binary alloys, PtCo displayed the highest activity towards molecular oxygen electroreduction followed by PtNi, PtZn, and PtCu. Although the activities for PtW, PtTi and PtSe are not the best of alloys investigated, these alloys do exhibit excellent chemical stability under our testing conditions and are therefore identified as promising alloy catalysts too.

By comparing alloy activity and stability in Fig. 1, the base metals may be described and categorized by the following two categories: (1) corrosive and active base metals including Co, Cu, Fe, Mn, Mo, Ni, V, and Zn; (2) stable and less active base metals such as Cr, Nb, Pd, Re, Se, Sn, Ta, Ti, W and Zr. A common feature for category 1 base metals is that only high Pt concentration compositions remain after stability testing indicating significant base metal corrosion, see Fig. 1. To further explore synergistic effects, stable metals were added to stabilize or passivate the active and corrosive binary alloys and, similarly, active metals were added to enhance the catalytic activities of stable and less active binary alloys. The results from these ternary alloy studies will be reported in the near future.

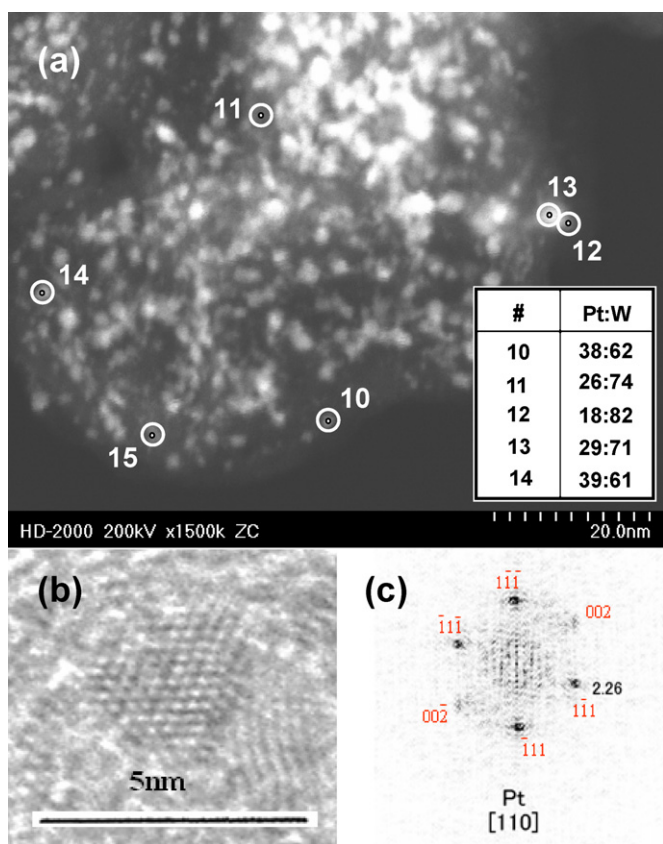


Fig. 2. (a) STEM image of carbon supported PtW nanoparticles synthesized by carbonyl complexes with microcomposition analysis; (b) lattice fringes; (c) fast Fourier transform analysis.

The relevance of using thin film screening of electrocatalysts as opposed to nano-powder screening is an issue under debate. Each methodology has merits and disadvantages. Thin films with desired compositions can be easily produced in the form of solid solutions; however, since films are not nanoscale, the nano-effect in catalysis cannot be observed. Alloy nanoparticles, on the other hand, are extremely difficult to synthesize with uniform micro-compositions, e.g. see [20–22]; therefore, most powder based screenings do not refer to the compositions claimed. Since PtW and PtTi films showed reasonable activities with relatively good chemical stabilities, carbon supported PtW and PtTi nanoparticles were synthesized using organometallic routines [28,29] to provide a fair comparison between thin film and powder results. Fig. 2(a) shows a typical STEM image of carbon supported PtW alloy nanoparticles synthesized by carbonyl complexes along with the microcomposition analysis performed using STEM-EDXS. The microcompositions among various nanoparticles are fairly uniform. The PtW nanoparticles have a predominantly spherical shape and are uniformly dispersed on the carbon support. Lattice fringes observed at higher magnification, Fig. 2(b), indicate that the alloy nanoparticles are well-crystallized. Fast Fourier Transform (FFT) analysis of the nanoparticles, Fig. 2(c), indicates that these nanoparticles have a FCC structure which agrees well with XRD results [28].

Fig. 3 displays the comparisons of relative mass specific activities between thin film and nanoparticle catalysts for PtW

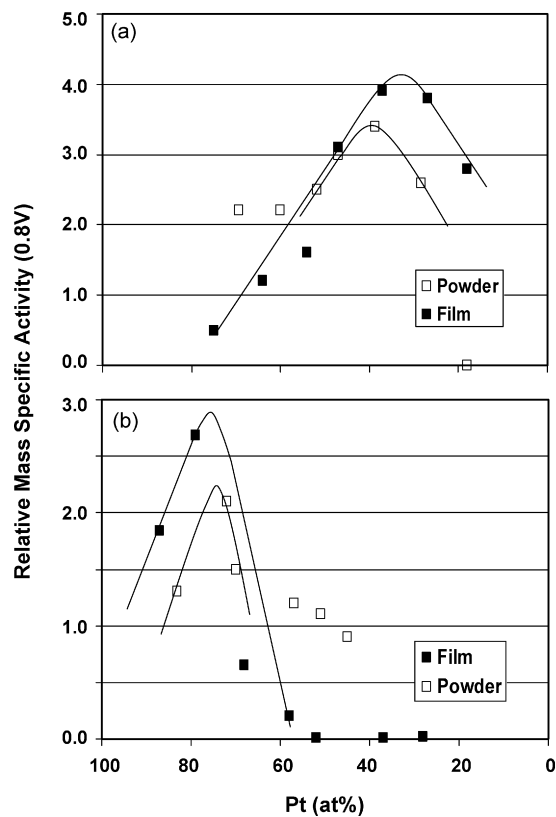


Fig. 3. Quantitative comparison of Pt mass-fraction/mass specific activities at 0.8 V between PtW thin film alloys and carefully engineered nanoparticles: (a) PtW; (b) PtTi.

and PtTi. Similar to most activity–concentration plots, volcano shapes were observed for both thin films and carefully engineered nanoparticles. Very good correlations were found between the thin films and the carefully engineered powders except that the activities are slightly lower for the powder samples and the activity peak positions of the nanoparticle catalysts are shifted a little bit. The difference in behavior between the thin films and nanoparticles may indicate a need for even better microcomposition uniformity.

The catalytic activity of an alloy can be described by:

$$\frac{J}{A \text{ g}^{-1}} = \frac{I_K}{A \text{ cm}^{-2}} \frac{S}{\text{cm}^2 \text{ g}^{-1}} \quad (1)$$

where I_K is the intrinsic current density and S is the active surface sites. The good correlations found between thin films and nano-powders indicate that it is appropriate to measure purely the intrinsic properties in electrocatalyst discovery. Considering the challenges of engineering nanoparticles with controllable size, monodispersity, and microcomposition uniformity, the thin film based high throughput screening developed here does offer remarkable advantages. The results of ternary alloys discovered by this combinatorial high throughput method will be reported soon.

4. Conclusion

By using the thin film based high throughput combinatorial tools, a systematic study of the electrocatalytic activity for oxygen reduction of various base metals alloyed with Pt was performed. Suitable alloy compositions were identified for each alloy system by considering the activity–stability–composition relationships in comparison with a pure platinum standard. Additionally, good activity correlations have been found between thin films and carefully engineered powders for PtW and PtTi alloys, indicating that the thin film based high throughput methodology is suitable for catalyst combinatorial screening.

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