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Combinatorial Methods for PEM Fuel Cell Electrocatalysts

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12.1 Introduction

12.1.1 Combinatorial Material Chemistry

Traditionally, chemists and material scientists rely on the slow and serendipitous trial-and-error process for discovering and developing new chemicals or materials. However, the conventional one-at-a-time, or one-by-one, methods are not capable of matching the pace of present-day material development. For example, in the area of drug discovery, it has been estimated theoretically that the number of possible drugs with molecular structures and weights attractive for pharmaceutical activity screening is 10^{18}. This number is $\sim 10^3$ times larger than the number of chemical substances available from commercial sources or in-house collections. This number is also $\sim 5\times 10^{10}$ times larger than that listed in the Chemical Abstracts Service (CAS) database. It is impossible to screen the pharmaceutical activities of such a large number of potential drugs by using traditional one-by-one methods. For organic substances, if each substance contains more than 30 atoms of H, C, O, N, and S elements, the number of potential stable molecular structures is expected to be $\sim 10^{63}$. For inorganic substances, possibilities include $\sim 3\times 10^3$ binaries, $\sim 7\times 10^4$ ternaries, $\sim 1\times 10^6$ quaternaries, and $\sim 6\times 10^{12}$ decanaries, which can be made from 75 useful and stable elements in the periodic table. These numbers exclude those with stoichiometric and structural diversity and different orders. Traditional one-by-one approaches will never be able to deal with the screening and optimization of these substances.

Fortunately, the situation began to change when a new field of chemistry, called combinatorial chemistry, arose in the late 1980s. Combinatorial chemistry is an innovative approach to speed up the discovery and development of new molecules and materials. The early successes of combinatorial chemistry in the pharmaceutical industry have been followed by the discovery of a wide variety of important materials in chemistry and materials science. These materials range from catalysts, polymers, and zeolites to luminescent and magnetoresistive compounds, agricultural materials, and high-temperature superconductors, dielectric, ferroelectric, and structural materials, as well as many others. Since Schultz and his group at the Lawrence Berkeley National Laboratory of UC Berkeley reported the usage of combinatorial methods for a search of superconductors in 1995, combinatorial chemistry has emerged as an exciting new paradigm for materials discovery. In the past two decades, this topic has attracted considerable scientific interest and research efforts in the fields of chemistry and material science.

In principle, the combinatorial method primarily includes two key steps: (1) combinatorial material libraries preparation and (2) high throughput chemical/physical screening. A combinatorial material library consists of many different samples with various compositions that are synthesized quickly, simultaneously, and in parallel. The combinatorial synthetic method contrasts with the time-consuming and labour-intensive traditional approaches, by which compounds are synthesized individually, one at a time. Through combinatorial methods, scientists can synthesize many hundreds or thousands of compounds at one time, instead of preparing only a few by a simple methodology. The combinatorial synthetic methods allow a very large number of substances to be synthesized much more rapidly and at lower cost than by traditional synthetic chemistry. High throughput screening is the process for rapid automated assessment of single or multiple properties of a large number of samples in the combinatorial libraries. Ideally, a useful high throughput screening method for combinatorial materials discovery should be capable of handling small-size samples with minimal sample preparation requirements, and should also have rapid turnaround in either serial or parallel analysis of library elements during or after the reaction and testing.

Basically, there are two different levels of combinatorial experiments: a discovery level and a focus level. A discovery level combinatorial screening is applied when totally new (alternative) materials are the targets of the search. The search motivation could be scientific curiosity and exploration of new materials. In some case, if the existing materials have no potential for further improvements, a discovery-level combinatorial screening may be used for alternative materials. This discovery screening can sample a broad and highly diverse range of parameter spaces. However, errors may occur because of the existing difference between combinatorial and conventional methods in synthesis and measurement conditions. Therefore, it is necessary to reproduce the materials resulting from the discovery screening by conventional synthesis, and confirm the expected function by conventional measurements. A focus-level combinatorial screening is used to accelerate the optimization process for material development. These materials could be either those revealed in the discovery screening stage or known materials. In these combinatorial experiments, relatively narrow and well-defined parameter spaces around known materials are sampled at high speed under conditions as close to the conventional experimentation conditions as possible. The goals of focus screening are to get reliable trends and optimized materials. Usually, systematic combinatorial work consists of both discovery and focus screening steps in order to achieve the goals of material development.

12.1.2 Electrocatalysis in PEM Fuel Cells

Proton exchange membrane (PEM) fuel cells are energy conversion devices, which operate by oxidizing a fuel (hydrogen or small organic molecules) at the anode and reducing oxygen at the cathode. In this process, a PEM is used as a separator between the anode and cathode, and also serves as an ionic conductor. The electrocatalysis in PEM fuel cells is mainly relevant to three kinds of fuel cell reactions: oxygen reduction reaction (ORR), hydrogen oxidation reaction (HOR), and methanol oxidation reaction (MOR), described as follows:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \tag{12.1}$$

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \tag{12.2}$$

$$CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^- \tag{12.3}$$

In a hydrogen-air/oxygen PEM fuel cell, electrocatalysts are necessary in order to catalyze the ORR (12.1) and HOR (12.2) at the cathode and anode, respectively. Normally, the ORR and HOR easily happen on the surface of noble metals such as platinum (Pt). However, in a hydrogen-fuelled PEM fuel cell, the reaction rate of the ORR is lower than that of the HOR by several orders. Therefore, the ORR at the cathode side dominates the overall performance of such a fuel cell. Thus, finding a good ORR electrocatalyst is one of the major subjects in PEM fuel cell electrocatalysis. To date, Pt is the most active and stable catalyst that can electrocatalyze the ORR at a practical rate in a PEM fuel cell. However, use of Pt is limited by its cost and rarity. In this sense, developing low or non-Pt ORR catalysts is highly desirable. There are two major strategies for cost-effective and high-performance catalysts: one is to lower Pt content in the catalysts through alloying other low-cost metals, without compromising performance; the other is to develop new non-Pt or even non-noble metal catalysts that are able to operate in a real fuel cell with acceptable activity and stability. For the HOR at the anode side, carbon monoxide (CO) as an impurity in the reforming hydrogen gas can poison the Pt surface, causing performance to drop. Even a very small amount of CO in the fuel can occupy and deactivate the Pt-active sites. Developing CO-tolerant catalysts for HOR is thus another R&D topic for hydrogen-fuelled PEM fuel cell electrocatalysis. Some platinum alloys such as PtRu have been found to be effective CO-tolerant catalysts for HOR.

In a direct methanol fuel cell (DMFC), the methanol oxidation reaction (MOR) is also a slow reaction in the whole electrochemical reaction process. Even using Pt as a catalyst, MOR is still much slower than HOR. The mechanism of MOR is much more complicated than those of ORR and HOR. The intermediates of MOR, including CO and CO-like species, can easily poison the Pt active site, causing large anode overpotential and then sluggish kinetics. Because liquid methanol is preferable to gaseous hydrogen, in terms of fuel storage and transportation, DMFC is thought to be the most promising fuel cell to be commercialized in the near future. A considerable global R&D effort in the DMFC community has been focused on cost-effective and high-performance catalysts for MOR. Lots of Pt-based alloys have been explored as candidates for MOR catalysis. In addition, ORR at the cathode can also be depressed due to the methanol crossover that happens when methanol penetrates the membrane. The methanol in the cathode will lead to a direct MOR between the cathode oxygen and the methanol on the Pt catalyst, depressing the concentration of oxygen. In addition, the resulting intermediates can also poison the Pt active sites. Both effects can cause performance degradation. Therefore, finding methanol-tolerant ORR catalysts for the DMFC cathode is also an important aspect of fuel cell electrocatalysis [7].

In the past several decades, numerous studies [5–8] have been carried out to address challenges in the area of fuel cell electrocatalysis. Many alloys, compounds, and composites have been explored and validated as effective fuel cell electrocatalysts, through traditional one-at-a-time study strategies. However, there is much room for new exploration of electrocatalysts, such as composition-diverse binary, ternary, quaternary alloys, or non-noble metal oxides and composites. It seems that the traditional methods for new catalyst development are not fast enough for electrocatalyst breakthrough to align with the urgent demands of fuel cell technology. Combinatorial chemistry thus provides a possible solution to the current need for fuel cell electrocatalysis R&D. Since Reddington et al. first introduced combinatorial electrochemistry into the field of fuel cell electrocatalysis in 1998, combinatorial methods have been rapidly developed and successfully applied to the high throughput screening of fuel cell electrocatalysts. Although still in their maturating period, combinatorial methods have been effective and promise great advantages for the discovery of new catalysts for fuel cell technology.

12.2 Combinatorial Methods for Fuel Cell Electrocatalysis

Similar to the applications of combinatorial chemistry in other fields, combinatorial methods for fuel cell electrocatalysis include two key procedures: preparing catalyst libraries, and high throughput screening of the chemical/physical properties of catalysts. The technical challenges for this new application involve how to transplant the existing combinatorial library preparation methods into the area of fuel cell catalysis, including considerations of array design and how to modify existing screening methods or develop new screening methods to match the electrochemical requirements of fuel cell catalysts.

12.2.1 Catalyst Library Preparation

12.2.1.1 Gradient Arrays

Mapping strategy is often used to design multi-element combinatorial libraries with a form of composition gradients. For example, in the pioneering work of Reddington et al., a quaternary combinatorial library was designed by unfolding a three-dimensional phase diagram to a two-dimensional map, as shown in Figure 12.1.

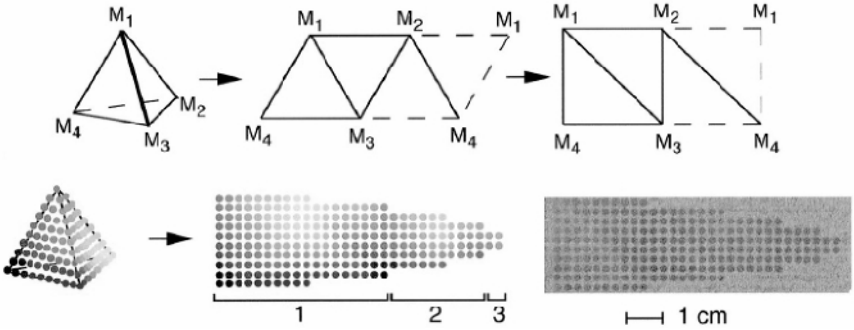


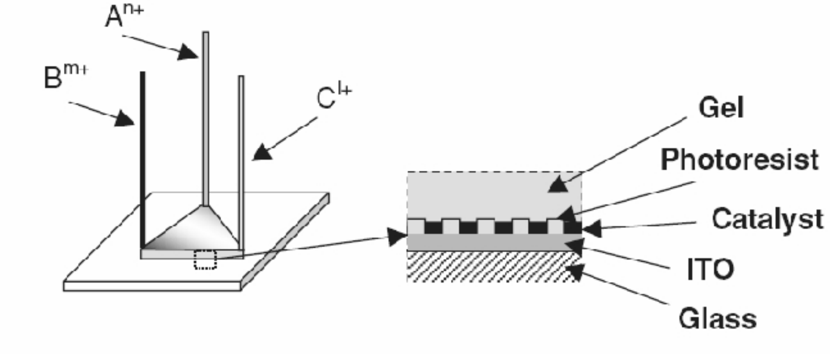
Figure 12.1. (Top) Unfolding of a quaternary phase diagram and mapping into two dimensions. (Lower left): at a resolution of 10 different compositions along each binary edge. This quaternary map contains 220 unique spots with composition varying smoothly across the array. Redundant binary lines (dashed lines in the top drawing) are eliminated in the map. The three nested shells in the phase diagram are marked by 1, 2, and 3 in the map. (Lower right): Inkjet-printed and subsequently borohydride-reduced array of electrocatalysts on Toray carbon paper [9]. (From Reddington E, Sapienza A, Gurau B, Viswanathan R, Sarangapani S, Smotkin ES, et al. Combinatorial electrochemistry: a highly parallel optical screening method for discovery of better electrocatalysts. Science 1998;280:1735–7. Reprinted with permission from AAAS.)

This mapping gives a smooth variation in composition across the array, as illustrated in the color map made from cyan, magenta, yellow, and black inks. According to the combinatorial theory, for a combinatorial map of n different components, the number of the total combinations N is given by Equation 12.4:

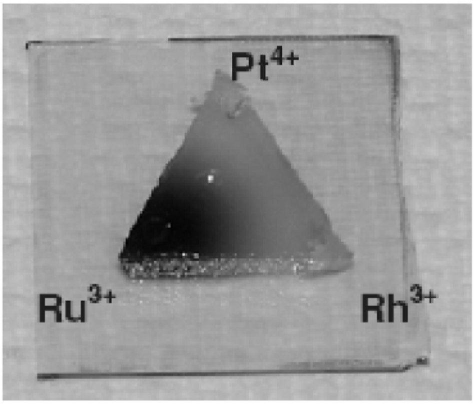
$$N(n,m) = \frac{(n+m-2)!}{(n-1)!(m-1)!} \tag{12.4}$$

where m is the number of compositions along a given binary edge in the map. In this case, $n = 4$, $m = 10$, so the total compositions $N = 12!/3!9! = 220$. It can be seen in Figure 12.1 that this quaternary array contains an outer shell of 4 elements (vertices), 48 binaries (edges), 112 ternaries (faces) and two inner shells containing 52 and 4 quaternaries. In total, there are 220 unique compositions. As shown in Figure 12.1, by customizing a commercially available inkjet printer with this quaternary pattern, the metal salt inks containing appropriate $H_2PtCl_6{\cdot}6H_2O$, $RuCl_3{\cdot}xH_2O$, $OsCl_3$, K_2IrCl_6, $RhCl_3{\cdot}2.4H_2O$ and glycerol were printed onto Toray carbon paper. After borohydride reduction of these metal salt inks, a quaternary combinatorial catalyst library with 220 samples was prepared.

Another preparation method for gradient array is “gel-transfer” electrodeposition, which was developed by Hiller and coworkers. This method involves the controlled diffusion of precursor metal salts into a hydrated gel from spatially distinct locations, followed by an electrodeposition to create a surface composition gradient. As illustrated in Figure 12.2(a), a ternary catalyst gradient was created by diffusing precursor metal salts, from three different locations, into a gel. A thin layer of 4% agarose gel was deposited onto a patterned ITO substrate. Glass capillaries were pierced through the gel at the three vertices of a triangle, through which the solutions of the metal salts were introduced. The metal salts were allowed to diffuse into the gel for several hours, a process which created a concentration gradient of the metal salts. The gel was then cut in the shape of a triangle and the metal ions were subsequently reduced onto the ITO surface by electrodeposition. The gel and photoresist were then removed, leaving a triangular-shaped three-component catalyst gradient on the ITO substrate. Figure 12.2(b) depicts a typical optical image of a concentration gradient of $Pt^{4+}/Ru^{3+}/Rh^{3+}$ ions within an agarose gel.



(a)



(b)

Figure 12.2. (a) Schematic of synthesis routine for a multi-component catalyst gradient by gel-transfer method. (b) Optical image of concentration gradient of $Pt^{4+}/Ru^{3+}/Rh^{3+}$ in agarose gel [12]. (Reproduced by permission of ECS—The Electrochemical Society, from Jayaraman S, Hillier AC. Electrochemical synthesis and reactivity screening of a ternary composition gradient for combinatorial discovery of fuel cell catalysts.)

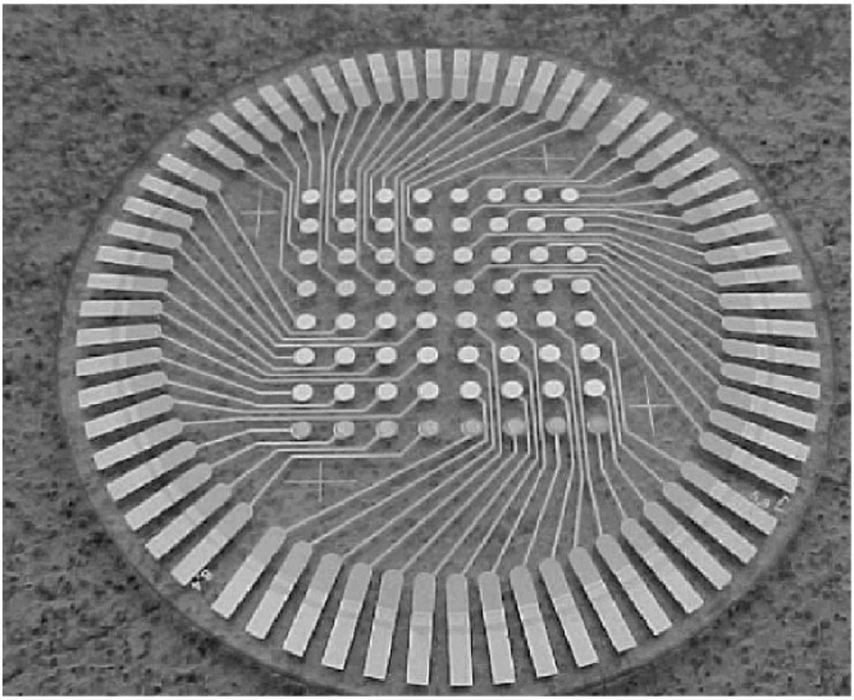


Figure 12.3. A 64-element addressable electrode array on a 3-inch quartz wafer which was used as a support for the synthesis of chemically diverse electrocatalyst libraries [13]. (Reprinted with permission from J Phys Chem B 2003;107:11013–21. Copyright 2003 American Chemical Society.)

12.2.1.2 Mask Arrays

Mask arrays are usually designed for the preparation of multi-metal alloys and oxides through the sputter deposition method. In a mask array, the catalyst compositions are controlled by designing the mask combinations. For instance, Strasser et al. invented a sputtering system for combinatorial studies of fuel cell electrocatalysis. A 64-element addressable electrode array was fabricated on an insulating 3-inch quartz wafer using lithographic techniques (Figure 12.3). Automated RF-magnetron vacuum sputtering was employed to rapidly synthesize the 64-element metal alloy electrocatalyst library (Figure 12.4[a]). The individual constituents of the synthesized catalyst composition were deposited onto the 64-element electrode array by controlling contact masks. A moving-shutter technique controlled the deposition process of thin-film gradients with ranges from a few Angstroms to several micrometers. Compositional variations in the thin films were achieved either by sputtering parallel and orthogonal thickness gradients or by sputtering multiple non-gradient metal slabs with varying thicknesses (Figure 12.4[b]). A ternary thin-film electrocatalyst library with the formulation of PtRuM (M=Co, Ni, W) was prepared using this technique.

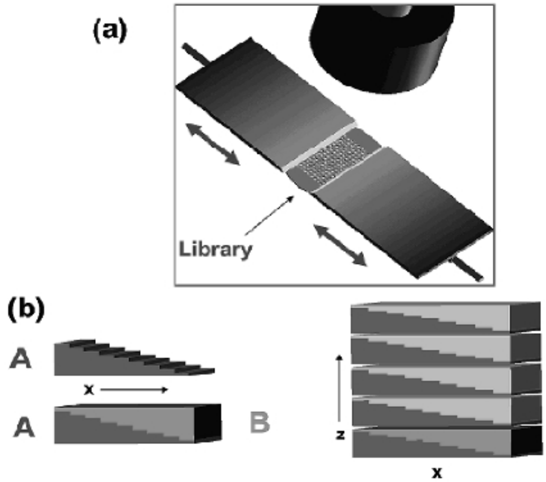


Figure 12.4. (a) An RF magnetron sputter technique with automated target selection, automated moving shutters, as well as physical shadow masking. (b) Sequential gradient sputtering of very thin material slabs which can lead to *in situ* formation of thin-film alloy on the contact spots. Superlattice deposition in z-direction can result in the build-up of thicker films of the desired stoichiometric gradient [13]. (Reprinted with permission from J Phys Chem B 2003;107:11013–21. Copyright 2003 American Chemical Society.)

12.2.1.3 Arrays of Conventional Electrodes

For some combinatorial experiments, in particular those focus-level combinatorial screening experiments, the number of experimental points is relatively low so that the high-resolution array designs can be fabricated by conventional catalyst preparation methods. For example, Guerin et al. adopted a traditional catalyst preparation method to fabricate a 64-element catalyst array for combinatorial electrochemical screening of fuel cell electrocatalysts, as shown in Figure 12.5. In this experiment, 8×8 glassy carbon rod electrodes were embedded in a glass-filled PTFE block. Volumetric suspensions of Pt/C powders containing Nafion in glacial acetic acid were manually deposited onto each electrode to form a 64-element catalyst array. The amount of Nafion in the deposits was controlled by adding 50 μL of 5 wt% Nafion suspension to the mixture of glacial acetic acid and Pt/C powder. In order to ensure the suspensions were homogeneous, the volumetric flasks containing these suspensions were vigorously shaken, using an ultrasound bath, for several hours prior to use. During the transfer of aliquots of the electrocatalyst suspensions, the volumetric flasks were immersed in the operating ultrasound bath throughout the process.

This preparation method of catalyst array has an advantage, which is that the high surface-area catalysts can be screened under similar circumstances as are used in the traditional half-cell electrochemical testing. An additional advantage is that through this approach, the effect of other chemical/physical variables besides composition can also be studied, for example, variables such as Pt loading and catalyst particle size, as has been done in Guerin's work.

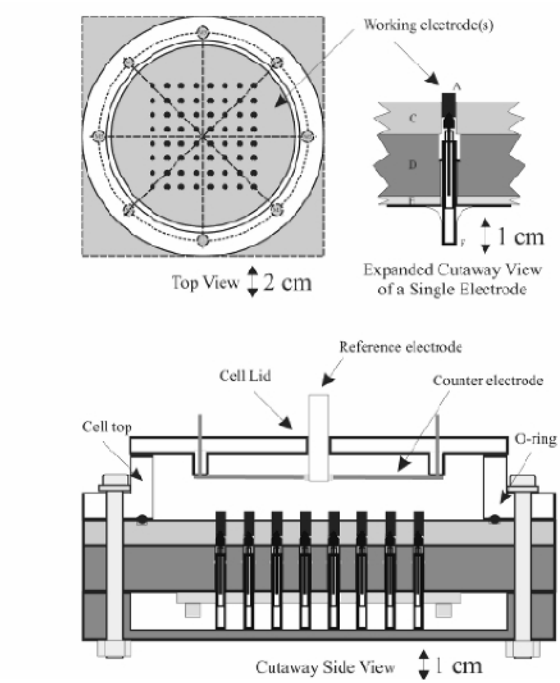


Figure 12.5. Schematic of the cell (viewed from the top, the side, and an expanded view of a single electrode) which was used for electrochemical screening of the 64-element array: (A) vitreous carbon electrode, (C) spring-loaded electrical contact, and glass filled PTFE array base plate, (D) polypropylene contact holder, and (E) a printed circuit board [14]. (Reprinted with permission from J Comb Chem 2004;6:149–58. Copyright 2004 American Chemical Society.)

12.2.2 Catalyst Activity Down-selection

12.2.2.1 Indirect Optical and Spectroscopic Screening

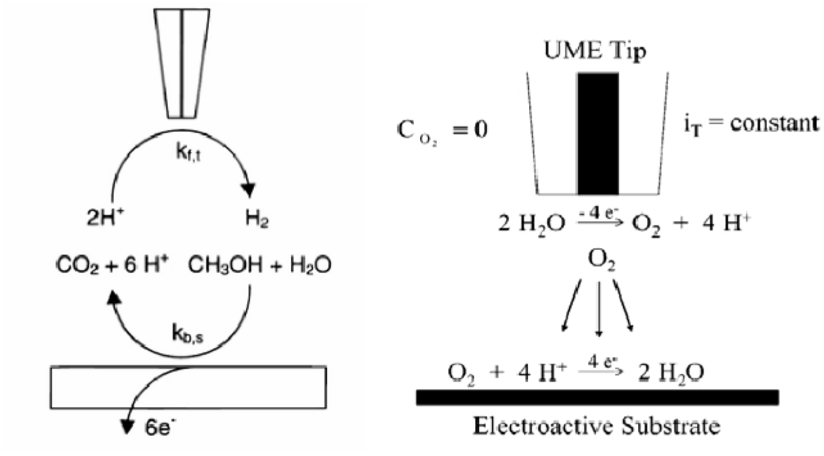
The optical detection method is widely used in combinatorial screening for biochemical affinity, organic host-guest interactions, and inorganic phosphorescence. The method is fast—regardless of the complexity of the array—simple to implement, and allows one to ignore the uninteresting majority of phase space. Reddington et al. [9] adopted this method for combinatorial screening of fuel cell electrocatalysts. They used a fluorescent indicator, quinine in a neutral solution, or NiPTP in a low pH solution to image the activity of the catalyst array. These chemicals are luminescent in their acid form. The fluorescent indicator could detect the presence of proton ions in the electrolyte, which resulted from the anodic methanol oxidation reaction. A typical example is illustrated in Figure 12.6, showing a Pt-Rh-Os ternary array screened in a 6 M methanol solution containing quinine indicator. The left shows an image in white light. The center shows a fluorescence image at low overpotential, displaying the most active region of composition space. To the right is a fluorescence image at high overpotential, with methanol oxidation occurring at every spot in the array. Based on optical observation, the best anode composition in this ternary array was found to be $Pt_{62}Rh_{25}Os_{13}$, which was much better than Pt but slightly inferior to $Pt_{50}Ru_{50}$.

Figure 12.6. A Pt-Rh-Os ternary array in 6 M aqueous methanol solution containing a quinine indicator [9]. (From Reddington E, Sapienza A, Gurau B, Viswanathan R, Sarangapani S, Smotkin ES, et al. Combinatorial electrochemistry: a highly parallel optical screening method for discovery of better electrocatalysts. Science 1998;280:1735–7. Reprinted with permission from AAAS.)

The greatest advantage of the optical method is simplicity when screening large catalyst libraries, because this technique requires only aqueous indicator solutions and a hand-held UV lamp. However, this method has two major drawbacks: it is insensitive to minor differences in electrode activity and it does not provide direct electrochemical measurement, which is required for complete characterization.

Scanning electrochemical microscopy (SECM) can also be treated as a combinatorial screening method for fuel cell electrocatalysis. Through positioning a microelectrode probe near a substrate-electrolyte interface, SECM has an ability to create mass transfer between the tip and the sample (proportional to their separation). The resulting mass transfer rate is high enough to evaluate fast kinetic rate constants. Typically, it can evaluate a kinetic constant with two to three orders of magnitude higher value than that evaluated by the regular ring-disk electrode (RDE) technique. In addition, SECM also can perform interfacial measurements as a function of spatial position, a function which allows direct structure-function measurements on the catalytic surfaces, through imaging variations in reactivity that occur in conjunction with changes in surface composition or structure.

There are primarily two SECM modes developed for combinatorial screening of fuel cell electrocatalysts. The first is the tip collection-sample generation (TC-SG) mode [16]. The principle of this mode was presented in Figure 12.7(a), with methanol oxidation as a model reaction. Normally, SECM employs a fine electrode tip that is moved near a surface through an x–y–z positioning system. When the tip scans near the surface, the electrochemical current between the tip and the substrate can be measured. In Figure 12.7, proton reduction was used as the SECM tip reaction. The protons were produced by hydrogen oxidation or methanol oxidation, then electrocatalyzed by the catalysts on the substrate. These protons were then reduced at the tip. If the tip potential value were to be made sufficiently negative, the reduction of protons would be at a diffusion-controlled rate. The variations in the tip current with the position could be used to characterize the relative reactivity of the substrate at different conditions, such as electrolyte, bias voltage, temperature, etc. This technique, combined with its electrochemical reaction mechanism, enables visualization of the spatial distribution of reaction rates across a catalyst library, thus aiding the search for new catalysts. One of the drawbacks of this method, however, is the pH limitation of the studied electrolyte. The other is the tip generation-sample collection (TG-SC) mode [17], which is targeted at the oxygen reduction reaction. The principle of this mode is shown in the Figure 12.7(b). In Figure 12.7, an ultramicroelectrode (UME) tip, controlled by the SECM, is placed close to the substrate and a constant oxidation current (i_T) is applied to the tip. Water is oxidized to oxygen on the UME, and a constant flow of oxygen is generated at the tip and diffused to the substrate. If the substrate potential is fixed at a value where oxygen should be reduced to water, the oxygen reached at the substrate surface will be reduced. The reduction rate of oxygen will be strongly dependent on the substrate potential and its electrocatalytic activity. The main advantage of this mode is that it can measure reactions inaccessible by the first mode, for example, the ORR in neutral or alkaline solutions. Figure 12.8 shows an example of SECM imaging of the ORR activities in a PtRu binary catalyst array.



(a) (b)

Figure 12.7. Scheme of (a) the tip collection-sample generation (TC-SG) mode [16], and (b) the tip generation-sample (TG-SC) collection mode [17] of SCEM combinatorial screening of fuel cell electrocatalysts. (Figure 12.7(a) reproduced by permission of ECS—The Electrochemical Society, from Shah BC, Hillier AC. Imaging the reactivity of electro-oxidation catalysts with the scanning electrochemical microscope. Figure 12.7(b) reprinted with permission from Anal Chem 2003;75:2967–74. Copyright 2003 American Chemical Society.)

Besides SECM, other spectroscopic methods, such as scanning differential electrochemical mass spectrometry (SDEMS) and IR thermography, were also used as combinatorial screening methods for fuel cell electrocatalysis. The principle of SDEMS is to use mass spectrometry to locally measure dissolved gases and volatile liquid species near the surfaces of catalyst arrays. IR thermography is based on reaction heat mapping. The heat results from the fuel cell electrochemical reactions on the catalyst arrays. Both methods can obtain reaction information that has an indirect relationship with the electrochemical reactions; therefore, similar to optical methods, they have the drawbacks of insensitivity. Furthermore, some special instruments are also required.

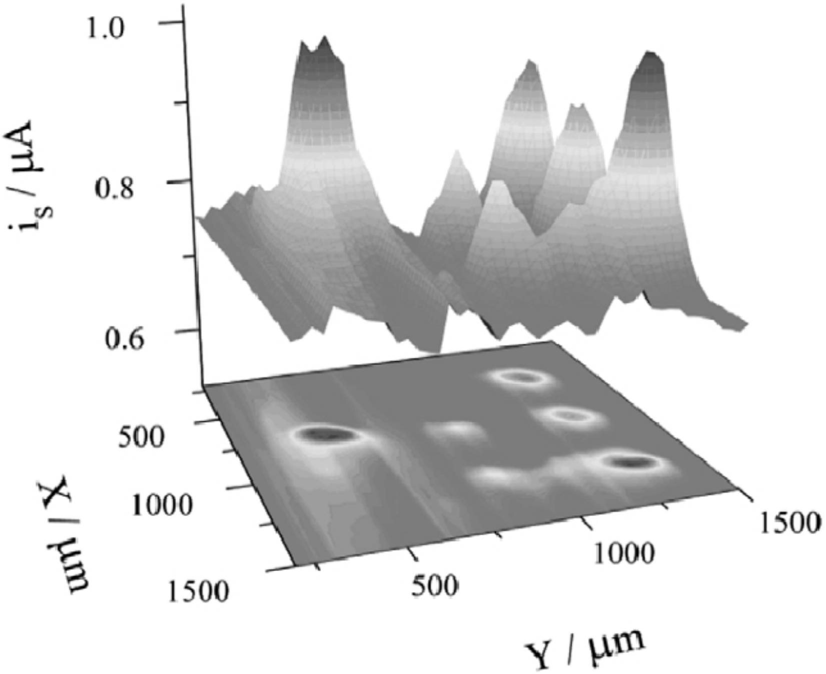


Figure 12.8. ORR images obtained by SECM (the TG-SC mode) screening of an array of Pt (left spot and right row) and Ru (middle row) spots supported on a glassy carbon [17]. (Reprinted with permission from Anal Chem 2003;75:2967–74. Copyright 2003 American Chemical Society.)

12.2.2.2 Direct Electrochemical Screening

The activity and performance of fuel cell electrocatalysts need to be evaluated in terms of electrochemical parameters, including current density and electrode potential. Electrochemical screening methods have been identified as ideal direct approaches for combinatorial studies of fuel cell catalysts. Two types of electrochemical measurement systems have been developed for combinatorial screening of fuel cell catalysts: the array half-cell system and the array single-cell system.

Figure 12.9 illustrates a typical array half-cell electrochemical screening system. In this system, the work electrode is a catalyst array that was prepared on a 2-inch silicon wafer with titanium nitride leads and pads, by the sputtering deposition technique. The catalyst array contains up to 100 combinatorial catalyst members. A glass cylinder and a silicone o-ring, both with a 38-mm diameter, are pressed on the wafer. In this way, the possible contact between the catalyst library pads and the electrolyte can be avoided. A plastic lid with a Teflon gasket is screwed on the assembly, fixing the entire cell in place. The whole array half-cell system contains the studied electrode array, an Nb (coated by Pt) counter electrode, a calomel reference electrode, a thermocouple, and an air stone. A multi-potentiostat connected to the target electrode array (working electrodes) was used for electrode potential control. All individual target electrodes in the array share the same counter electrode and reference electrode. Cooper and McGinn [22] successfully applied this system to combinatorial screening of two ternary Pt-Ru-W and Pt-Ru-Co catalyst series for methanol oxidation reaction. In addition, the 64-element array electrochemical screening system developed by Guerin et al. [14] (shown in Figure 12.5) is also a good example of the array half-cell system for electrocatalyst combinatorial screening.

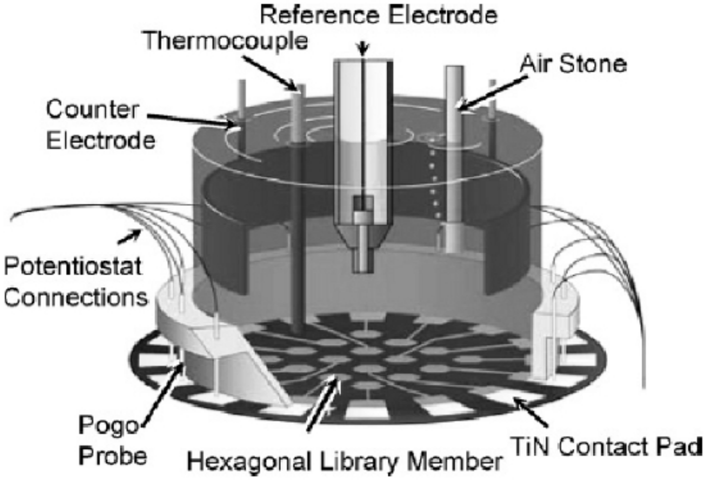


Figure 12.9. Schematic drawing of an assembled electrochemical cell for combinatorial screening catalyst libraries prepared by sputter deposition [22]. (Reprinted from Journal of Power Sources, 163(1), Cooper JS, McGinn PJ. Combinatorial screening of thin film electrocatalysts for a direct methanol fuel cell anode, 330–8, ©2006, with permission from Elsevier.)

Figure 12.10 shows an array single-cell electrochemical system, which was invented by Liu and Smotkin for electrocatalyst combinatorial screening in a real fuel cell circumstance. This array single-cell electrochemical system contains 25 individually controllable electrodes. Each electrode represents a miniaturized fuel cell: gaseous or liquid fuel can be introduced through fuel cell array flow fields. The catalyst layers were fabricated in exactly the same manner as for fuel cells. The fabrication methods used for the preparation of state-of-the-art membrane electrode assembly (MEA) were employed for the fabrication of the catalyst array, allowing catalyst testing with realistic reactant exposure histories (conditioning) and steady-state reaction conditions. The individual catalysts were prepared by traditional ink deposition technique and applied onto carbon paper. Array disks were punched and hot-pressed onto the Nafion membrane. For electrochemical measurements, a standard fuel cell counter electrode was used. In order to provide a large area and non-polarizable reference electrode, hydrogen gas was delivered to the common cathode. The graphite sensor electrodes were pressed and inserted into the insulating ceramic flow field. Polarization curves for all array targets were recorded simultaneously using a multi-potentiostat. This array single-cell electrochemical system has a unique advantage over other combinatorial screening methods, in that its testing conditions are very close to the real fuel cell circumstances.

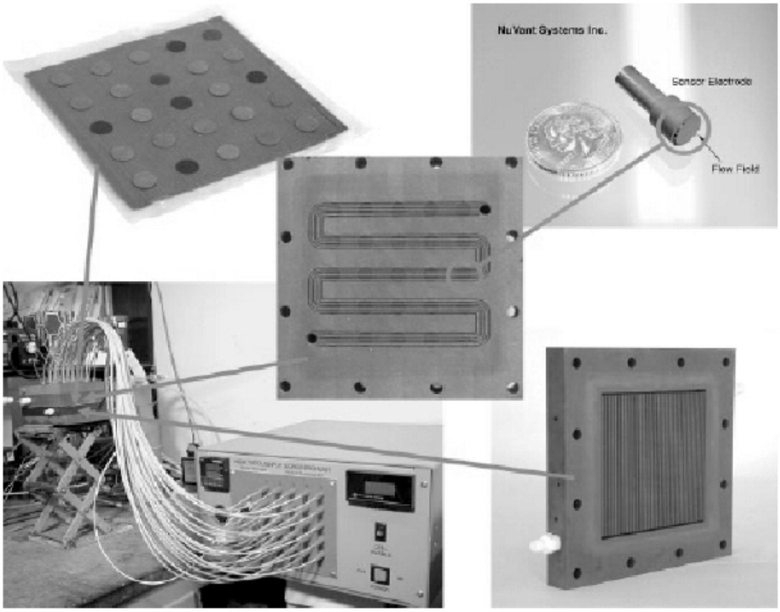


Figure 12.10. Component of array fuel cell: array flow field (center), clockwise from upper right: array MEA, graphite flow field sensor, counter electrode flow field, and assembled cell with multielectrode potentiostat [15]. (Reprinted, with permission, from the *Annual Review of Materials Research*, Volume 33 ©2003 by Annual Reviews www.annualreviews.org.)

12.3 Combinatorial Discoveries of Fuel Cell Electrocatalysts

Since Reddington et al. [9] first applied combinatorial electrochemistry to screen quaternary platinum alloys for DMFC anodes, many electrocatalysts, including noble metal alloys, non-noble metal alloys, metal oxides (perovskite), transition metal chalcogenides, as well as transition metal macrocycles, have been explored by these combinatorial methods for fuel cell electrocatalysts. Besides element screening and composition optimization, combinatorial methods were also useful in investigating the synthesis and reaction conditions, such as Nafion content in MEA inks, Pt loading in the catalyst layer, Pt particle size, sintering temperature, metal dissolution, and so on. Here, we describe several typical examples of using combinatorial methods to develop new electrocatalysts for PEM fuel cell reactions.

12.3.1 Low/Non-platinum Content Catalysts for PEM Fuel Cell Cathodes

Developing low or non-platinum content catalysts for ORR at the cathode is one of the major challenges in overcoming the cost barrier for PEM fuel cell commercialization. Two major approaches for this subject are: (1) alloying other noble or non-noble metals into Pt, and (2) exploring Pt-free metal compounds as effective and stable ORR electrocatalysts. There are a large number of new alloys and compounds that may be suitable for this purpose, although so far few new catalysts have been found to match the goal.

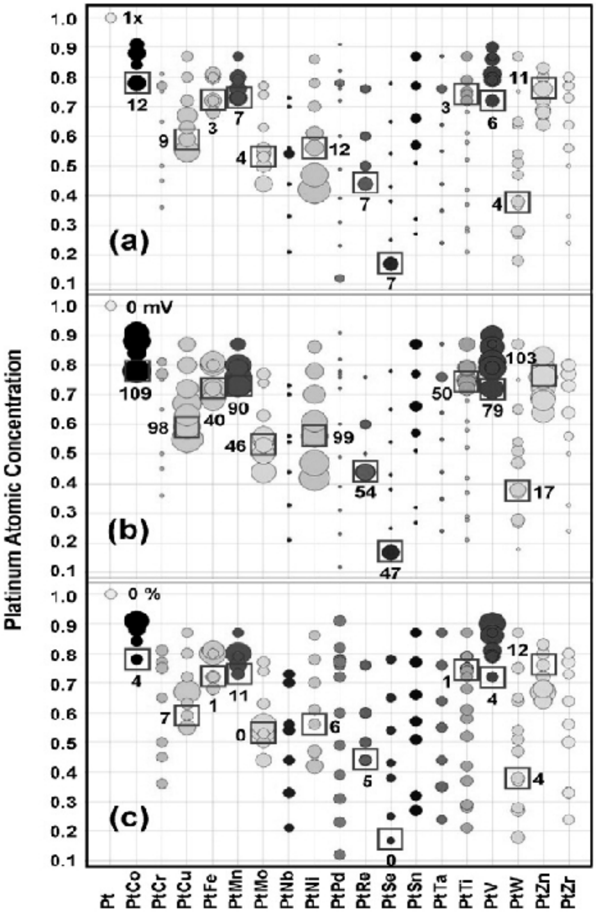


Figure 12.11. (a) Relative Pt mass-fraction specific activities at 0.8 V for Pt binary alloys; (b) half-wave potential (HWP) shifts of these alloys in comparison with pure Pt standard; (c) relative changes of Pt atomic concentration of these alloys after electrochemical corrosion testing [24]. (Reprinted from Journal of Power Sources, 165(1), He T, Kreidler E, Xiong L, Ding E. Combinatorial screening and nano-synthesis of platinum binary alloys for oxygen electroreduction, 87–91, ©2007, with permission from Elsevier.)

Compared to traditional methods, combinatorial methods show powerful capability for exploring such a huge number of catalyst candidates. For example, He et al. recently applied a multi-source physical vapor deposition technique to fabricate a series of binary Pt alloy thin film arrays, and employed a high throughput combinatorial screening for down-selection of a wide range of Pt-based binary alloy electrocatalysts for ORR. The candidates of these Pt-based binary alloy catalysts contained 18 base metals (Co, Cu, Fe, Mn, Mo, Ni, V, Zn, Cr, Nb, Pd, Re, Se, Sn, Ta, Ti, W, and Zr). Their catalyst array was electrochemically screened by a hydrodynamic multi-rotating disk electrode (M-RDE) system, which consists of 16 stations. Each station has a typical three-compartment electrochemical cell configuration, containing a conventional rotator (working electrode), a glass cell, a counter electrode, and a reference electrode. Using a multi-channel potentiostat, ORR reactions on all individual working electrodes in the array were measured simultaneously in oxygen-saturated 0.5 M H_2SO_4. The screening results were compared with a pure platinum baseline in terms of activity, stability and composition relationships. As shown in Figure 12.11, PtCo, PtNi, PtZn, and PtCu display higher catalytic activities towards oxygen electroreduction, but have poorer chemical stability in acid electrolytes. Alloys based on PtW, PtTi, and PtSe offer some modest catalytic activity improvements but have better chemical stabilities. These results are consistent with previous results obtained by the conventional one-at-a-time method, and also provide useful hints in exploring new ternary or quaternary alloy ORR catalysts with high activity and good stability.

12.3.2 CO-tolerant Catalysts for PEM Fuel Cell Anodes

Developing CO-tolerant Pt alloy catalysts for HOR at the fuel cell anode is also important in reducing the technical difficulties of purifying hydrogen fuel. At the current stage of technology, reforming hydrogen gas is more cost-effective than pure hydrogen. However, impurities (such as CO) in reforming gas can easily poison the catalysts. It has been identified that the poison effect could be minimized through alloying other metals with Pt catalysts. For example, PtRu shows much better CO-tolerance than pure Pt. Therefore, searching for more effective and cheaper CO-tolerant catalysts for HOR is necessary. Recently, Yang et al. demonstrated the effectiveness of combinatorial methods in studying the multi-element alloying effect of catalysts on the PEM fuel cell hydrogen oxidation reaction. $Pt_{1-x}M_x$ (M = Ru, Mo, Co, Ta, Au, Sn), randomly alloyed catalysts with a wide range of binary composition covering, were fabricated by DC magnetron sputtering technique. The catalyst activities were studied in a 64-electrode single-cell system using pure hydrogen or reformate that contained up to 50 ppm CO as fuel. When pure hydrogen was used, most of the binary compositions in the $Pt_{1-x}Ru_x$, $Pt_{1-x}Mo_x$, and $Pt_{1-x}Co_x$ samples were found to be better HOR catalysts. The HOR overpotentials when using $Pt_{1-x}Ta_x$, $Pt_{1-x}Au_x$, and $Pt_{1-x}Sn_x$ as catalysts were increased significantly if the compositions were at intermediate metal levels (Ta and Au > 50 atom. %, Sn > 40 atom. %). This implies that the alloying elements can significantly degrade Pt catalytic activity towards HOR. If the reformate was used as fuel (shown in Figure 12.12), Ru, Mo, and Sn were found to improve the CO tolerance of Pt catalysts, although the intrinsic HOR catalytic activity of Pt decreased significantly with increasing Sn content. The addition of Co to Pt had no impact on CO tolerance, possibly due to the Co loss through dissolution during the fuel cell operation. The addition of Au to Pt led to an increase in HOR overpotential when CO was present. Small amounts of Ta gave a small reduction in HOR overpotential in the presence of CO, but the overpotentials were still too high for practical application in a reformate-fed fuel cell.

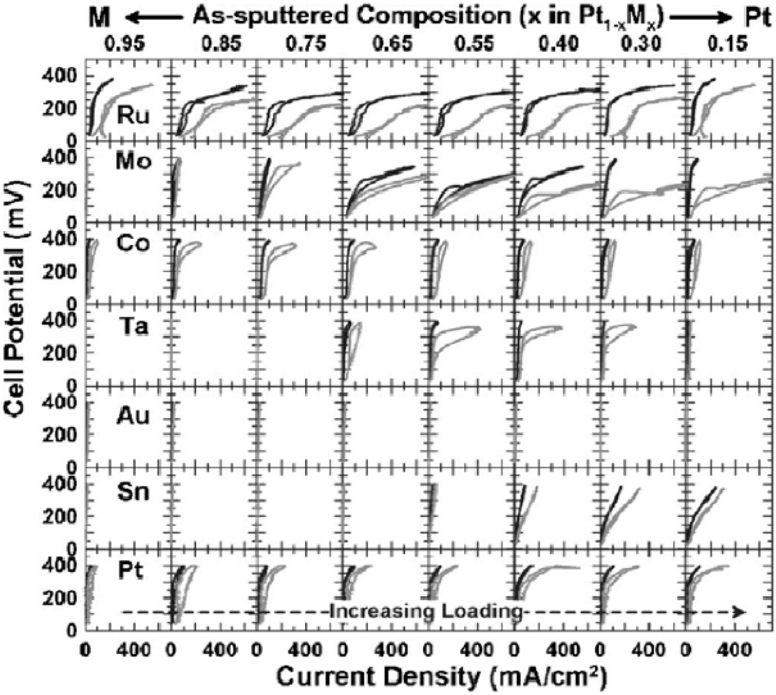


Figure 12.12. Representative CO-tolerance hydrogen oxidation polarization for the six binary systems studied. The measurements were made with (gray lines) 10 ppm and (black lines) 50 ppm CO in reformate fuel (40% H_2, 21% CO_2, 39% N_2) [25]. (Reproduced by permission of ECS—The Electrochemical Society, from Journal of the Electrochemical Society, Yang R, Bonakdarpour A, Bradley Eaton E, Stoffyn-Egli P, Dahn JR. Characterization and PEMFC testing of $Pt_{1-x}M_x$ (M=Ru,Mo,Co,Ta,Au,Sn) anode electrocatalyst composition spreads.)

12.3.3 Platinum Alloy Catalysts for Direct Methanol Fuel Cell Anodes

One large advantage of DMFC over the hydrogen fuel cell is the use of more manageable liquid methanol instead of hydrogen as fuel. However, the sluggish kinetics of the methanol oxidation reaction (MOR) leads to lower performance than in the H_2-fuelled PEMFC. Thus, developing high-efficiency MOR catalysts has attracted a great deal of attention in recent years. PtRu alloys have been identified as the best catalysts, so far, for MOR at DMFC anodes. In fact, the first application of combinatorial methods to fuel cell catalyst screening is the exploration of new quaternary Pt alloy catalysts for DMFC anodes. A quaternary alloy, $Pt_{44}Ru_{41}Os_{10}Ir_5$, was found to be much more active than the state-of-the-art $Pt_{50}Ru_{50}$ catalyst if it was used as a DMFC anode catalyst, even though the latter catalyst had about twice the surface area of the former [9]. Following this pioneer work, many studies have been carried out using combinatorial methods to screen DMFC anode electrocatalysts. Cooper et al. [22] employed a sputtering technique to fabricate a series of ternary alloy catalyst libraries, and adopted an array half-cell electrochemical system to combinatorially investigate the Pt-Ru-W and Pt-Ru-Co ternary alloy systems as DMFC anode electrocatalysts. They found that the addition of W and Co into the Pt-Ru alloy had a positive effect on the DMFC performance. However, a change in optimum composition with the potential cycling of the electrode was observed. Initially, $Pt_{25}Ru_0W_{75}$ and $Pt_{17}Ru_{17}Co_{66}$ had 3 and 20 times better performances than the best binary Pt-Ru catalyst, respectively. However, after cycling the potential at 60 °C, the optimum ternary compositions were shifted from $Pt_{25}Ru_0W_{75}$ to $Pt_{44}Ru_{12}W_{44}$ and from $Pt_{17}Ru_{17}Co_{66}$ to $Pt_{12}Ru_{50}Co_{38}$, respectively, as shown in Figure 12.13. The optimum Pt-Ru-W and Pt-Ru-Co compositions show a peak MOR current density that was 1.5 and 2.5 times more than the best Pt-Ru binary composition, respectively. These results were different from those reported in other studies. The deviation was probably due to differences in the catalyst synthesis methods.

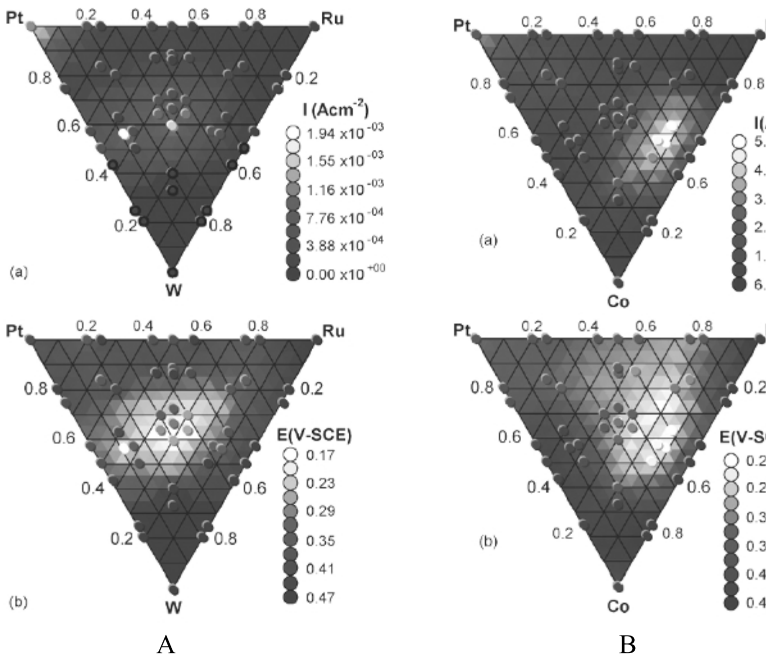
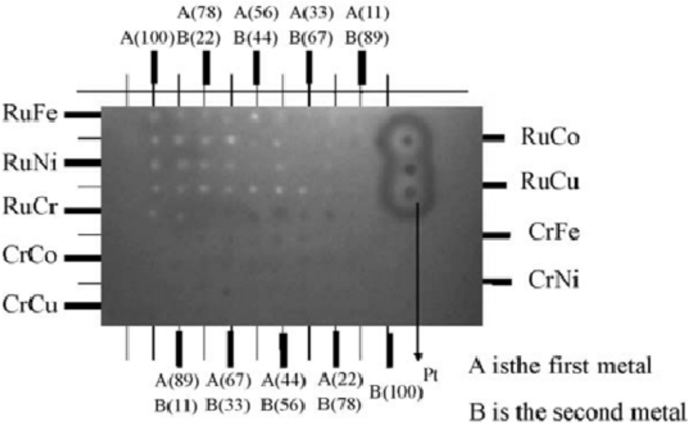
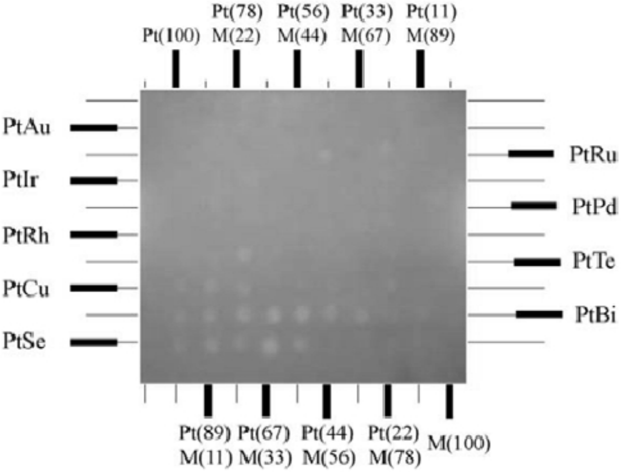


Figure 12.13. (a) Peak current densities and (b) onset potentials of methanol oxidation reaction electrocatalyzed by the combinatorial (A) Pt-Ru-W and (B) Pt-Ru-Co systems. [22]. (Reprinted from Journal of Power Sources, 163(1), Cooper JS, McGinn PJ. Combinatorial screening of thin film electrocatalysts for a direct methanol fuel cell anode, 330–8, ©2006, with permission from Elsevier.)



(a)



(b)

Figure 12.14. Fluorescence image of Pt and non-Pt binary array at 0.55 V vs. RHE in oxygen saturated electrolyte (pH = 4), which contained 100 mM fluorescein sodium salt, 0.2 M $NaNO_3$ and 0.5 M methanol [26]. (Reprinted from Applied Surface Science, 252(7), Liu JH, Jeon MK, Woo SI. High-throughput screening of binary catalysts for oxygen electroreduction, 2580–7, ©2006, with permission from Elsevier.)

12.3.4 Methanol-tolerant Catalysts for Direct Methanol Fuel Cell Cathodes

Combinatorial methods have also been applied to the area of exploring methanol-tolerant Pt and non-Pt alloy catalysts for DMFC cathodes. Liu et al. investigated a series of Pt-based and non-Pt binary alloys as ORR electrocatalysts by employing the high-throughput optical screening method. The catalyst arrays were prepared by ink deposition technique, using an automatic dispenser followed by a thermal treatment. The ORR activities were evaluated in oxygen-saturated sulfuric acid containing 100 mM of fluorescein sodium salt as pH indicator. As illustrated in Figure 12.14, some of the Pt-based binary catalysts, including PtBi, PtCu, PtSe, PtTe, and PtIr, as well as the non-Pt catalysts, such as RuFe, show higher activities than pure Pt. All the active binary catalysts exhibit better methanol tolerance than Pt. In particular, the RuFe catalyst has a stronger methanol tolerance capability. Moreover, stability tests showed that after polarizing the binary arrays at 1.0 V in 1 M H_2SO_4, the obtained fluorescence images displayed the same brightness as those before polarization, suggesting that these binary catalysts were stable. This stability may suggest that the binary catalysts currently developed could be suitable candidates for PEM fuel cell or DMFC cathode catalysts, although further validation is necessary in real fuel cell operation.

12.4 Conclusions

Electrocatalysis is one of the important areas in PEM fuel cell development and commercialization. Although numerous researchers have been successful, over the past several decades, in searching for new fuel cell electrocatalysts, there are still large technical and cost gaps that need to be closed with respect to the commercialization of PEM fuel cells, including DMFCs. In order to speed up catalyst development, the combinatorial method has been identified as an effective way for new catalyst exploration and development. Since it was first introduced into fuel cell electrocatalysis ten years ago, the combinatorial method has developed rapidly and has shown significant advances in applications of fuel cell electrocatalysis. Many combinatorial catalyst library preparation methods (such as ink-jet printing, sputtering, electrodeposition, and traditional ink deposition) and high throughput screening methods (such as optical detection, electrochemical half-cell array, electrochemical single-cell array, SECM, SDEMS, and IR thermography) have been designed, invented, and improved. Various noble metal or non-noble metal alloys, compounds, and composites have been explored as candidates for electrocatalysts of major PEM fuel cell reactions, including ORR, HOR, and MOR.

However, the current combinatorial techniques still have some limitations for fuel cell catalyst synthesis and screening. The main drawback is that the current combinatorial catalyst libraries (gradient arrays and mask arrays) fabricated by high-speed and large-capacity preparation methods are not comparable to the traditional catalysts synthesized by state-of-the-art techniques. The differences between the synthetic methods may lead to different optimum compositions. In some rare cases, false information may lead to mistakes in interpreting results.

Hence, for the further development of combinatorial methods in PEM fuel cell catalysis, improving the catalyst library preparation techniques is significant. It is also suggested that a complete combinatorial study of fuel cell electrocatalysis may include both discovery level and focus level experiments, where the catalyst libraries are fabricated by both high throughput methods and traditional methods, respectively. And eventually, the optimal catalysts should be validated in real fuel cell testing.

It is worth noting that combinatorial chemistry has only been explored in the field of fuel cell electrocatalysis for a short time (around ten years). Therefore, it is still a developing and maturing technology. With improvement in both catalyst library preparation and screening techniques, combinatorial methods will become more important in new fuel cell electrocatalyst development. It is also believed that this combinatorial method will speed up new catalyst exploration, and thus accelerate developments toward PEM fuel cell breakthrough and commercialization.

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