

Combinatorial Discovery of Alloy Electrocatalysts for Amperometric Glucose Sensors

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Combinatorial methods were used to search for active alloy electrocatalysts for use in enzyme-free amperometric glucose sensors. Electrode arrays (715-member) containing combinations of Pt, Pb, Au, Pd, and Rh were prepared and screened by converting anodic current to visible fluorescence. The most active compositions contained both Pt and Pb. Bulk quantities of catalysts with compositions corresponding to those identified in the screening experiments were prepared and characterized. The best alloy electrocatalysts catalyzed glucose oxidation at substantially more negative potentials than pure platinum in enzyme-free voltammetric measurements. They were also insensitive to potential interfering agents (ascorbic and uric acids, and 4-acetamidophenol), which are oxidized at slightly more positive potentials. Rotating disk electrode (RDE) experiments were carried out to study the catalytic mechanism. The improvement in catalytic performance was attributed to the inhibition of adsorption of oxidation products, which poison Pt electrodes.

Because of the importance of reliable and fast monitoring of blood sugar for the treatment and control of diabetes, the development of amperometric glucose sensors has been a subject of concern for decades.¹ Most studies on this subject have involved the use of the enzyme glucose oxidase, which catalyzes the oxidation of glucose to gluconolactone. In most glucose sensors, the enzyme is contacted by a redox mediator, which is reduced by the enzyme and reoxidized at the surface of an electrode. Alternative designs use enzymes that are internally “wired” with mediators that access the flavin cofactor of glucose oxidase electrochemically.² In other glucose sensors, oxygen is reduced by the enzyme to hydrogen peroxide, which is oxidized at an electrode surface. While the latter sensors have the advantage of easy and controllable fabrication, they operate at relatively positive potentials, at which some interfering agents, such as ascorbic and uric acids, can contribute to the observed current. This overpotential can be lowered by using noble metals such as platinum,³ rhodium,⁴ and gold,⁵ which exhibit preferential electrocatalytic

activity toward peroxide. In all cases the anodic current of the glucose sensor is linked to the enzymatic reaction and varies linearly with the concentration of glucose in a certain range.⁶

The principal disadvantage of essentially all glucose sensors is the requirement for an enzyme, which is the least durable part of the sensor. Unfortunately, eliminating the enzyme places some severe constraints on the electrocatalyst, which must perform a multielectron oxidation reaction in the presence of easily oxidized interfering agents. The electro-oxidation of glucose on noble metals such as platinum⁷ and gold⁸ has been studied in the hope that an effective enzyme-free sensor could be made. In glucose solutions, platinum electrodes lose their activity quickly by accumulation of chemisorbed intermediates, which block the electrocatalyst surface. Another disadvantage of noble metal electrodes is that they lack the inherent selectivity of glucose oxidase, that is, various organic substances can be oxidized on these electrode surfaces.

A possible solution to these problems is to use alloy electrocatalysts, which combine the electrochemical properties of their components. Although we might expect some such alloys to be good catalysts that resist poisoning, there is little theoretical or experimental guidance for predicting their compositions a priori. Also, as the number of elemental components increases, the number of possible compositions to be tested grows geometrically. Under the circumstances, combinatorial screening methods are a natural choice for catalyst discovery.⁹ Recently, we developed a rapid combinatorial synthesis and screening method for the evaluation of methanol fuel cell anode catalysts.¹⁰ Glucose sensing presents a similar problem, and in many ways a simpler one, because complete oxidation of glucose (to CO₂) is not required. This paper reports the extension of our combinatorial method to the search for alloy electrocatalysts for amperometric glucose sensors. The best compositions found not only catalyze glucose

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oxidation very near the formal potential of the half-cell reaction in enzyme-free, pH-neutral solutions but also are insensitive to interfering agents, such as ascorbic acid, uric acid, and 4-acetamidophenol (acetaminophen), which are oxidized at slightly more positive potentials.

EXPERIMENTAL SECTION

Materials. Toray carbon paper was purchased from Electro-Chem, Inc. Vulcan XC-72 carbon black was purchased from Cabot Corp. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and Na_2PdCl_4 were purchased from Alfa Aesar and used as received. D-Glucose, L-ascorbic acid, uric acid, 4-acetamidophenol, and soluble Nafion perfluorinated ion-exchange resin were used as received from Aldrich. Glucose stock solutions were allowed to mutarotate overnight before use. Nanopure water (18 M Ω -cm) was used to prepare all solutions. All other chemicals were analytical grade and were used as received from commercial sources.

Synthesis and Screening of Combinatorial Arrays. Pentanary electrode arrays (715-member) were prepared by automatically delivering aqueous metal salt solutions onto a piece of Toray carbon paper sandwiched between gaskets of a home-built multiwell template, using a programmed Aspirate and Dispense System (Cartesian Technologies). The system utilizes step-motor-controlled syringe pumps and micro-solenoid valves to dispense aqueous solutions with 10 nL/spot accuracy. The arrays were dried overnight in air and were reduced under flowing hydrogen at 250 °C for 1 h.

The arrays were sandwiched into a screening cell, which exposed the alloy spots to an aqueous solution containing glucose, electrolyte, and a fluorescent indicator (quinine). Electrical contact was established to make the array the working electrode of a conventional three-electrode electrochemical cell with a saturated calomel electrode (SCE) reference and platinum gauze counter electrode. The screening solution (0.2 M glucose, 0.2 M NaClO_4 , 100 μM quinine, pH \approx 7) was then added to the cell. The working electrode potential was increased in 25–50 mV steps, beginning at a potential of –250 mV vs SCE, with a hand-held UV lamp (366 nm) above the surface of the electrode array. The array was typically held at each potential for 1 min. Fluorescent spots were detected by eye at each potential.

Preparation of Bulk Catalysts and Modified Electrodes. Bulk catalysts with the compositions discovered in the screening experiment were prepared as follows: First, metal salt precursors in the desired stoichiometry were mixed in an aqueous solution with 33 wt % carbon black, which had been made hydrophilic by reaction with 4-aminobenzenesulfonic acid. The mixture was then dried and reduced under flowing hydrogen at 200–250 °C, and crushed with a mortar and pestle. Catalyst inks were prepared by adding 740 μL of Nanopure water and 60 μL of 5% Nafion solution to a vial containing 15 mg of dry catalyst. The slurry was stirred overnight. Then 2 μL of the catalyst slurry was carefully applied to the surface of a freshly polished, 2 mm diameter glassy carbon electrode and dried at room temperature.

Electrochemical Characterization of Bulk Catalysts. Electrochemical experiments were carried out with a BAS 100B/W Electrochemical Workstation (Bioanalytical Systems, Inc.). The catalyst-modified glassy carbon electrode, a reference electrode (SCE or mercurous sulfate electrode (MSE)) and a platinum wire

auxiliary electrode entered a 10 mL electrochemical cell (model VC-2, BAS) through holes in its PTFE cover. Cyclic voltammetry was done while gently purging the headspace of the cell with Ar after first bubbling to deoxygenate the solution. Rotating disk electrode (RDE) experiments were carried out with RDE electrode (model AFMR 28, Pine Instruments) secured to an analytical rotator (Model AFMSRX, Pine Instruments).

Characterization of Bulk Catalysts. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MPD diffractometer, using monochromatized $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. X-ray photoelectron spectra (XPS) were obtained with a Kratos XSAM 800 PCI spectrometer, which had a $\text{Mg K}\alpha$ line source. Powder samples were mounted on carbon tape, and spectra were obtained with a 40 eV pass energy, and at a 15° takeoff angle from the surface normal.

RESULTS AND DISCUSSION

Combinatorial Screening of Alloy Electrocatalysts. Although combinatorial synthesis and screening techniques were originally developed for materials discovery,¹¹ they have not been widely used in these applications until quite recently. The renaissance of combinatorial materials chemistry has followed from its very successful application to biological and pharmaceutical problems, and from the subsequent development of automated synthesis and screening methods for materials.⁹ Recently, there have been a few reports of combinatorial methods applied to electrochemical problems. In electrochemical reactions, one can detect current directly in a multielectrode array,¹² or indirectly by converting current to an optical signal by means of fluorescent indicators.¹⁰ Our work has employed the latter technique, which is experimentally simpler and more easily scaled to very large combinatorial libraries, but less quantitative than the direct detection method.

Our previous papers described the use of discrete arrays containing combinations of one, two, three, and four elements.^{10,13} Those electrode arrays mapped a quaternary (three-dimensional) composition space at a resolution of 10 discrete spots along each binary edge, giving a total of 220 unique catalyst compositions per array. In the present work, we expanded this approach to pentanary (five-element) combinatorial libraries, which at the same resolution provide the five pure elements and all combinations of two, three, four, and five elements in a 715-member array. As before, the catalyst arrays were made with the constraint that each spot contained the same total number of moles of metal. The mapping and fabrication strategies were similar to those previously described,^{10,13} except that a commercial plotter (rather than an ink-jet printer) was used to deliver metal salt solutions to the Toray carbon backing of the electrode array.

The electro-oxidation of glucose has been studied for decades. Although the details of the electrode reaction are not completely understood, in all proposed mechanisms the oxidation reaction generates protons.⁷ In unbuffered electrolytes, a drop of several pH units should occur at the surface of active catalyst spots. The

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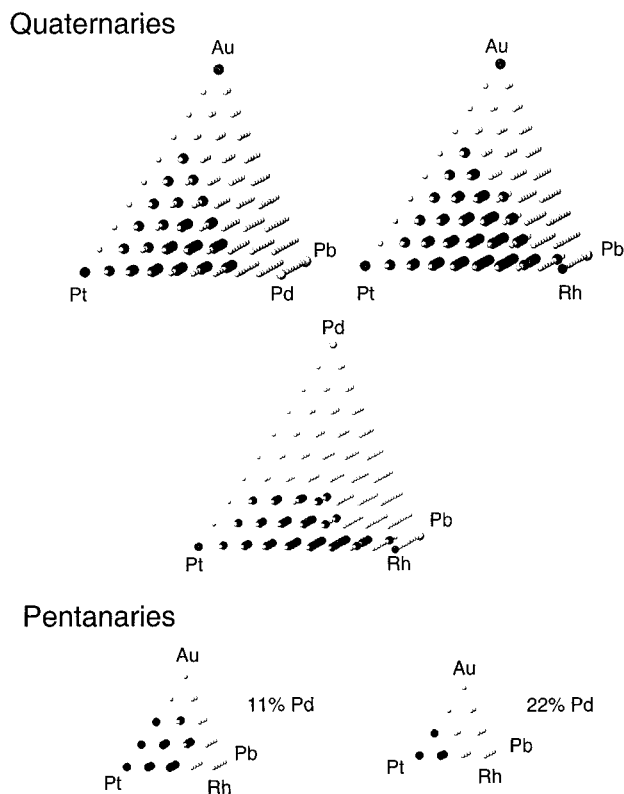


Figure 1. Screening results for Pt–Pb–Au–Pd–Rh alloy catalysts. Active compositions for glucose oxidation are shown as dark spots. Only three of the five quaternary regions (those containing both Pt and Pb, top) contained active catalysts. (Bottom) Tetrahedral sections of the pentanary part of the composition map.

initial pH of the solution was adjusted to between 7 and 8, and quinine, which has a pK_a of 5.5 and is strongly fluorescent in its acid form, was used as the indicator. Active electrode compositions showed visible blue fluorescence at moderate overpotentials under UV illumination. In the screening experiments, the arrays were initially held at a potential where no glucose oxidation occurred (-250 mV vs SCE), and were then stepped to increasingly anodic potentials in 25–50 mV increments. The arrays were held at each potential for about 1 min. Visible fluorescence was observed for active compositions, starting at about +250 mV versus SCE. Triplicate arrays were tested and showed good reproducibility. The screening experiments were carried out in unbuffered solutions, and because fluorescence occurs at a local pH that is below the pK_a of the indicator ($pH \leq 5$), the onset of fluorescence is found at relatively positive potentials. Experiments conducted with the same catalysts in pH neutral buffered solutions gave more negative current onsets (see below).

Figure 1 shows a catalytic activity map for the Pt–Pb–Au–Pd–Rh composition space. Because a pentanary composition diagram is a four-dimensional simplex, it is represented in Figure 1 by its five quaternary (tetrahedral) “surfaces”, which contain 645 of the 715 spots in the array, and by tetrahedral cuts through the 70-spot pentanary region. Only regions that contained active catalysts are shown in the Figure. In general, these were Pt-rich compositions that also contained Pb, and therefore the two quaternary tetrahedra that lacked Pt or Pb contained no active catalysts. There are regions of activity near the Pt vertex of each part of the diagram shown in Figure 1, although pure Pt, which

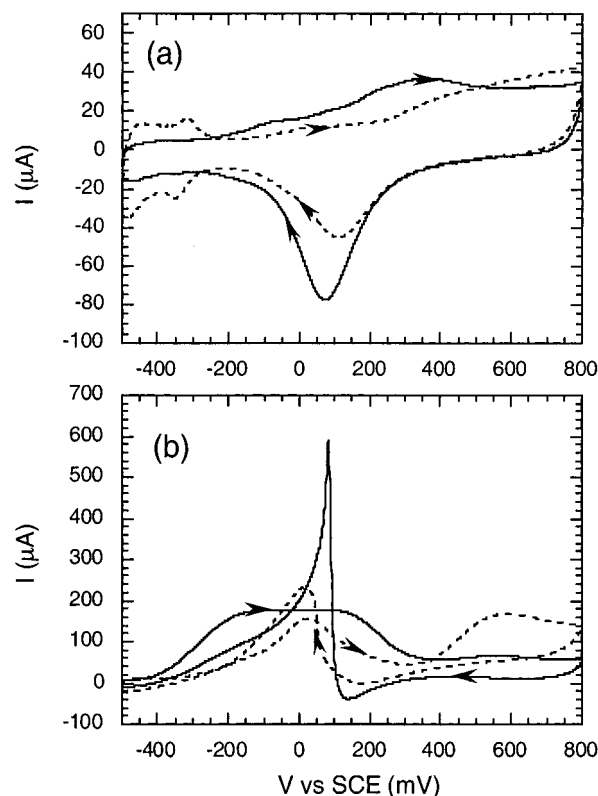


Figure 2. Cyclic voltammograms of 2 mm diameter Pt-modified (dashed line) and Pt_2Pb -modified (solid line) electrodes (a) in 0.1 M phosphate buffer, and (b) in 0.1 M phosphate buffer containing 0.1 M glucose. Quiescent solutions were deoxygenated before acquiring data. Scan rate: 10 mV/s.

is quickly poisoned, is not among them. These results show that both Pt and Pb play key roles in the process of glucose oxidation, although neither is a good catalyst by itself. Further, the screening experiments suggest that a broad range of binary, ternary, quaternary, and pentanary compositions have roughly comparable catalytic activity for this reaction.

Electrochemical Characterization of Bulk Catalysts. Combinatorial searches identify the active regions of composition space, but more detailed testing is needed to verify the activity, stability, and selectivity of catalysts under real use conditions. Representative catalysts from Figure 1 (Pt_2Pb_1 , $Pt_4Pb_2Rh_2Pd_1$, $Pt_4Pb_2Rh_3$, $Pt_4Pb_2Au_2Rh_1$, $Pt_4Pb_2Rh_2Au_1$, $Pt_4Pb_2Pd_2Au_1$, $Pt_9Au_9Pb_9Rh_5Pd_4$, subscripts indicate atomic ratios) were therefore prepared in bulk form and tested electrochemically in glucose solutions. For these experiments, the alloy catalysts must adhere to the electrode surface, and catalyst-modified electrodes prepared under the same conditions should give reproducible results. The proportions of water, alloy catalyst, and soluble Nafion were therefore optimized to prepare a reproducible catalyst “ink”. An adherent, uniform film could be formed by applying 2 μ L of this ink, which contained ~ 38 μ g of alloy catalyst, to the surface of a glassy carbon electrode.

Figure 2 compares cyclic voltammograms of pure Pt and one of the alloy catalysts discovered in the screening experiments, Pt_2Pb , in phosphate buffer with and without glucose. The voltammogram of Pt in phosphate buffer is characterized by its well-known hydrogen adsorption/desorption waves at negative potentials, a flat double layer region at intermediate potentials, and Pt

oxide formation/reduction waves at positive potentials. In contrast, the hydrogen adsorption/desorption waves are fully suppressed at Pt₂Pb in the same buffer. A new anodic peak appears at +400 mV versus SCE, corresponding to Pb dissolution.¹⁴ In the presence of glucose, two anodic waves attributed to the oxidation of glucose are observed at 0 and +550 mV versus SCE in the positive scan at Pt. In the negative scan, the oxidation of glucose is suppressed because of the presence of a surface oxide, which is reduced at potentials negative of about +200 mV. An anodic wave corresponding to glucose oxidation is again observed in the negative scan at Pt once the oxide layer is reduced.

The voltammetry of Pt₂Pb in glucose solutions (Figure 2b) is markedly different from that at Pt. The first glucose oxidation wave is observed at substantially more negative potentials than at Pt, and the current onset is at approximately -400 mV versus SCE. This anodic wave is very broad, implying a mechanistically complex oxidation process. The current is substantially higher than at Pt, especially at low overpotentials. This observation is consistent with the screening results, which showed high currents (high fluorescence) for Pt₂Pb and alloys of similar composition at low overpotential. The voltammetry at Pt₂Pb shows some other interesting features. In the Pt oxide region, glucose oxidation is inhibited. Upon reduction of the surface oxide, there is a sharp increase in anodic current on the negative scan, consistent with the high activity of the catalyst. It is interesting to note that most of the active catalyst compositions shown in Figure 1 gave similar results, that is, a shift in the first oxidation wave toward more negative potentials and a considerable increase in the current density in this wave.

Glucose oxidation at Pt electrodes suffers from serious poisoning resulting from a stable adsorbate that blocks the active sites of the electrocatalyst surface.⁷ Although it has been suggested that this adsorbate is gluconolactone (which is the product of enzymatic glucose oxidation), experiments with both Pt₂Pb and Pt electrodes gave essentially the same results as those shown in Figure 2b when 0.02 M gluconolactone was added. It is unlikely, therefore, that the oxidized species blocking the catalytic Pt surface is gluconolactone. It has been shown that underpotential deposition (UPD) of heavy p-block elements, such as Tl, Pb, and Bi, causes pronounced catalytic effects on the anodic oxidation of glucose at Pt.^{14,15} The role of adsorbed heavy element submonolayers on Pt electrodes is believed to be the suppression of hydrogen adsorption. The formation of surface hydride species are implicated in the conversion of glucose to its surface-bound oxidation product. Unfortunately, these UPD-modified electrodes are unstable as glucose sensing anodes because the p-block element is anodically stripped as glucose is oxidized. Because of the suppression of hydrogen adsorption found in Figure 2a, it is reasonable to conclude that Pb in Pt₂Pb and related alloys plays a similar role. However, these alloys have acceptable stability in the potential range where they are used for glucose sensing, because the glucose and Pb oxidation waves (Figure 2) are separated by several hundred millivolts.

Rotating disk electrode experiments were carried out to verify the hypothesis that electrode poisoning occurs at Pt, but not at

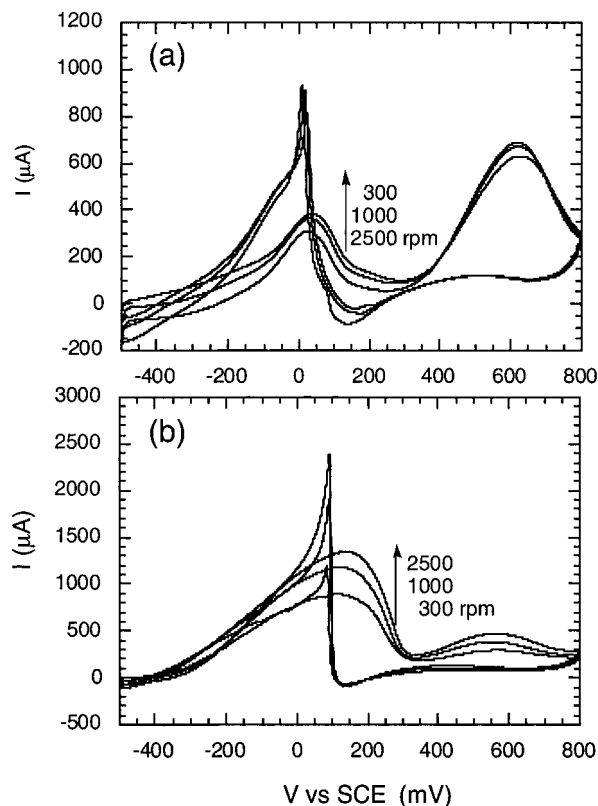


Figure 3. Cyclic voltammograms of (a) Pt- and (b) Pt₂Pb-modified electrodes in 0.1 M phosphate buffer containing 0.1 M glucose, obtained under hydrodynamic conditions. Rotation rates are indicated in the figure. Scan rate: 5 mV/s

Pt–Pb alloy electrode surfaces, in glucose solutions. Figure 3 shows cyclic voltammograms obtained at slow scan rate and three different rotation rates. The current in the first anodic wave, attributed to glucose oxidation, decreases with increasing rotation rate at a Pt-modified RDE. In contrast, the current in the same wave increases with increasing rotation rate at the alloy electrode. Increasing the rotation rate increases the flux of glucose to the surface, and in the case of Pt this causes more rapid adsorption of molecules that poison the catalyst. Consequently, the electrode is more quickly poisoned in the positive scan at high-rotation rates. At the alloy electrode, poisoning is not significant, and increased mass transfer results in increased anodic current.

Chemical Sensing and Interferences. For chemical sensing applications, electrocatalysts are generally evaluated by measuring current at fixed potential and time after addition of the analyte and possible interfering agents.^{3–5} Figure 4 compares the amperometric response of Pt₂Pb- and Pt-modified electrodes at -150 mV versus SCE with successive increments in the glucose concentration. After each addition of glucose to the stirred solution, the current at Pt₂Pb increases rapidly and then decreases to a relatively constant value. In the case of Pt electrodes, only the first few additions of glucose generated a measurable response. Subsequent additions gave only small signals, and the total response decreased continuously, because of the electrode poisoning noted above. These data confirm that pure Pt is not a stable electrode material for the constant-potential detection of

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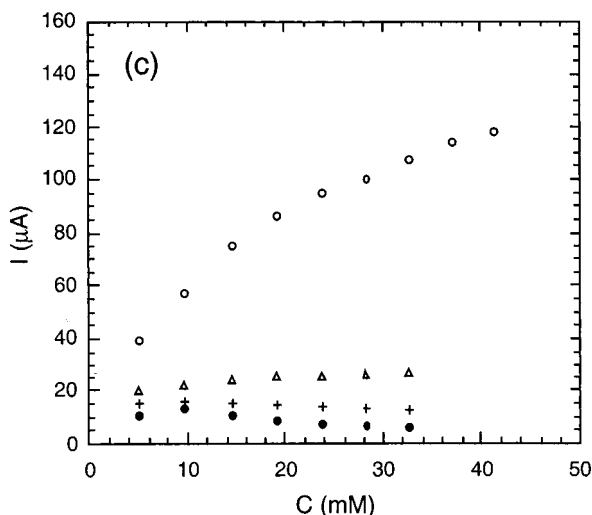
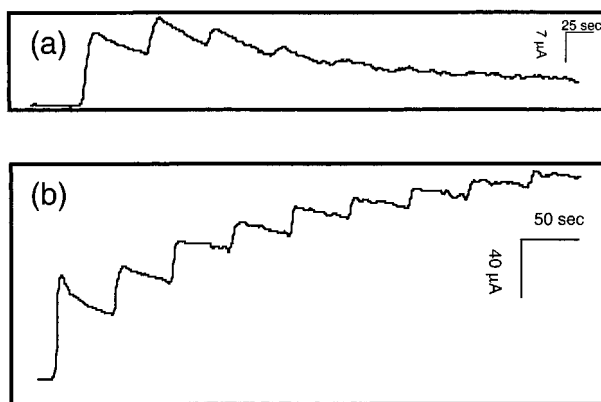


Figure 4. Current–time response for successive additions of 0.2 mL of 0.5 M glucose/0.1 M phosphate to 20 mL 0.1 M phosphate buffer at (a) Pt- and (b) Pt₂Pb-modified electrodes. The solution was deoxygenated with Ar and stirred magnetically during data acquisition. (c) Plot of plateau current just before the next glucose addition vs total glucose concentration at Pt- (●,+) and Pt₂Pb-modified electrodes (○,△). Operating potential: -150 mV vs SCE. Supporting electrolytes: 0.1 M phosphate buffer (●,○); 0.36 M NaHCO₃, 0.01 M NaCl, 0.001 M Na₂HPO₄ (+,△).

glucose.¹⁶ On the other hand, Pt₂Pb showed much higher currents at this potential (note the different current scales in a and b), and the response was stable and reproducible. A calibration curve (Figure 4c) shows that the current at the alloy electrode increases monotonically over the range of physiological interest (0–10 mM) for glucose sensing. As is expected for Pt and Pt alloy electrodes, chloride has a serious poisoning effect on the electrocatalysis. The current is almost entirely suppressed by addition of 0.01 M NaCl, and there is little variation of current with glucose concentration.

As noted in the introduction, the elimination of interference by easily oxidizable compounds is a real challenge in amperometric glucose detection, particularly for sensors that do not take advantage of the inherent selectivity of glucose oxidase. Because Pt₂Pb and related alloy catalysts oxidize glucose at very negative potentials, these interferences can be effectively eliminated. Figure 5 compares the voltammetric responses of a Pt₂Pb-modified electrode in a glucose solution and in a solution of one of the

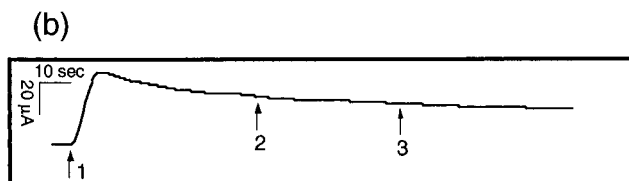
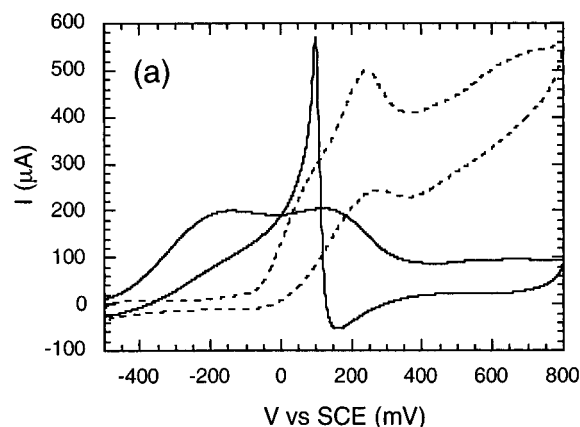


Figure 5. (a) Cyclic voltammograms of a Pt₂Pb-modified electrode in 0.1 M ascorbic acid (dashed line) and 0.1 M glucose (solid line) in 0.1 M phosphate buffer. Scan rate: 10 mV/s. (b) Current–time trace for a Pt₂Pb-modified electrode with addition of 5×10^{-3} M glucose (1), 1×10^{-4} M 4-acetamidophenol (2) and 1×10^{-4} M ascorbic acid. Electrode potential: -150 mV vs SCE.

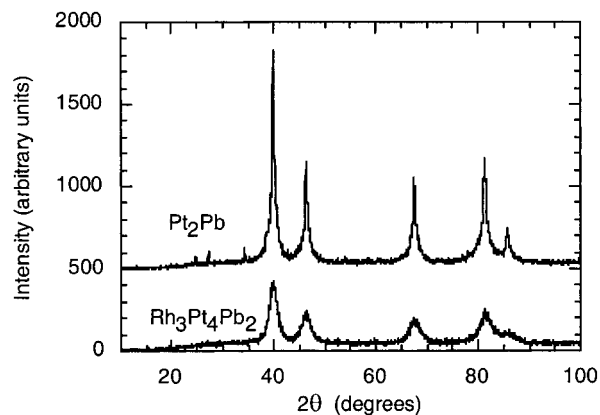


Figure 6. Powder X-ray diffraction patterns of Pt₂Pb and Rh₃Pt₄Pb₂.

more common interfering agents, ascorbic acid. The onset of ascorbic acid oxidation is positive of -100 mV versus SCE. With a poor catalyst, such as Pt, this interference is difficult to avoid; however, a good catalyst can operate at more negative potentials and is therefore insensitive to ascorbate at normal concentrations. Figure 5b demonstrates the selectivity of a Pt₂Pb-modified electrode, with successive additions of glucose, 4-acetamidophenol, and ascorbic acid. As expected, the glucose response is not affected by the presence of these two potential interfering agents. A separate experiment gave similar results for uric acid.

Physical Characterization of Alloy Catalysts. Figure 6 shows powder XRD patterns for two representative alloy electrocatalysts, Pt₂Pb and Pt₄Pb₂Rh₃. As prepared, the patterns of the alloy catalysts show only a nanocrystalline face-centered cubic phase. The primary particle sizes, determined from the line widths by

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Table 1. XPS Binding Energies and Apparent Surface Compositions of Alloy Catalysts

catalyst	apparent atomic ratio (binding energy, eV)		
	Pt 4f	Pb 4f	Rh 3d
Pt ₂ Pb	2.5(71.4)	1.0(138)	
Pt ₄ Pb ₂ Rh ₃	4.5(71.5)	3.6(138)	1.0(308)

means of the Scherrer equation,¹⁷ are 3.9 nm for Pt₄Pb₂Rh₃ and 15.5 nm for Pt₂Pb. The particle size of Pt prepared under the same conditions is 9.6 nm. Since both alloys are substantially better electrocatalysts than pure Pt for glucose oxidation, and since there are only small differences between the activities of Pt₂Pb, Pt₄Pb₂Rh₃ and the other active alloys tested, it can be concluded that the improvement in catalytic activity is not a simple consequence of particle size.

Surface atomic compositions of these catalysts, derived from XPS spectra, and XPS binding energies are shown in Table 1. Within experimental error, there is no evidence for surface enrichment in either Pt or Pb in Pt₂Pb. Overlap of the Rh 3d peak with Pt 4d and the C 1s electron energy loss peak makes quantitation of surface Rh difficult. The Pt 4f binding energy is in the range expected for metallic Pt (71.2 eV) and is substantially lower than that of PtO (73.8 eV) and other oxidized Pt compounds. However, the Pb 4f peak corresponds more closely to oxidized forms of Pb (PbO, 138.9; Pb₃O₄, 138.0) than to metallic Pb (136.4 eV). It is not known if surface Pb is in the oxidized state as prepared, or if it is oxidized in the air thereafter. Also, under electrochemical conditions (at -150 mV vs SCE), the data in Figure 2a suggest that Pb is most likely reduced to the zero oxidation state.

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CONCLUSIONS

We have shown that a combinatorial method originally developed for the discovery of fuel cell electrocatalysts can also be used effectively in the search for better sensor materials. Sensor electrocatalysts present an easier problem in many respects, because complete oxidation of the analyte is not required, and other requirements of a fuel cell catalyst (optimized mass transport and catalyst utilization) are less important in sensor applications. Although we have examined only glucose in this study, it is conceivable that amperometric sensors for a wider range of chemically and biochemically interesting analytes could be improved by this technique.

A broad range of binary, ternary, and higher Pt–Pb alloy compositions resist poisoning in glucose solutions and allow glucose to be sensed amperometrically at potentials negative of the oxidation of common interfering agents. Additional work is needed to fully understand the surface composition of these catalysts and its relation to the catalytic reaction mechanism. However, our results are consistent with previous observations that the suppression of hydrogen adsorption on Pt inhibits the formation of strongly adsorbed products of glucose oxidation. The most serious limitation of the alloy catalysts discovered in this work is their sensitivity to poisoning by chloride, which is likely to be present in most applications of glucose sensors. Future work will involve screening of alloys in the presence of chloride to determine if there are ranges of alloy compositions that are more resistant to poisoning.

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