Combinatorial electrochemical synthesis and screening of Pt-WO$_3$ catalysts for electro-oxidation of methanol

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An automated system for high-throughput electrochemical synthesis and screening of fuel cell electro-oxidation catalysts is described. This system consists of an electrode probe that contains counter and reference electrodes that can be positioned inside an array of electrochemical cells created within a polypropylene block. The electrode probe is attached to an automated of X-Y-Z motion system. An externally controlled potentiostat is used to apply the electrochemical potential to the catalyst substrate. The motion and electrochemical control are integrated using a user-friendly software interface. During automated synthesis the deposition potential and/or current may be controlled by a pulse program triggered by the software using a data acquisition board. The screening includes automated experiments to obtain cyclic voltammograms. As an example, a platinum-tungsten oxide (Pt-WO$_3$) library was synthesized and characterized for reactivity towards methanol electro-oxidation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1927007]

I. INTRODUCTION

Fuel cells have attracted considerable attention in the past few decades due to changes in the global oil scenario and a shift in focus towards cleaner and renewable sources of energy and the associated energy conversion technologies.$^1$ Hydrogen is the simplest of fuels that can be employed in fuel cells,$^2$ but due to the inherent difficulties in production, storage, handling, and distribution of pure hydrogen, it cannot be used economically in practical fuel cells.$^3$ Reformate hydrogen (which invariably contains CO as impurity) and other liquid organic fuels such as methanol, ethanol, etc. are considered as pragmatic alternatives to pure hydrogen.$^4,5$ Direct methanol fuel cells (DMFCs) have particularly attracted attention in recent years due to their promise as compact, low-temperature power sources not dependent on hydrogen.$^6$

Methanol electro-oxidation is a six-electron transfer reaction involving successive dehydrogenation followed by oxidation of –CO to CO$_2$. The serial mechanism consists of several intermediates including –CH$_3$O, –CH$_2$O, –CHO, and –CO. Platinum is the best catalyst for electro-oxidation of methanol among single-component catalysts.$^5$ However, the intermediates formed during the dehydrogenation reactions adsorb strongly to the Pt sites, poisoning them and preventing further oxidation of methanol. To overcome the poisoning, overpotential for methanol oxidation is required, which decreases the performance of the DMFC. Thus, catalyst poisoning is a major obstacle in the use of DMFCs in practical applications.

There have been several efforts directed at using multicomponent catalysts for methanol oxidation. When alloyed with Pt, metals including ruthenium, iridium, molybdenum, osmium, rhodium, tin, etc. have been shown to improve its electro-oxidation activity.$^8,9$ Many of these elements are believed to improve the poison tolerance of Pt through a bifunctional mechanism in which the alloyed metal forms surfaces oxides at low potentials which oxidatively remove the adsorbed species from Pt. Another possible mechanism that has been advocated is that the alloyed metals change the electronic structure of Pt such that the bond strength of the adsorbed intermediates on Pt is reduced, resulting in more facile oxidation.$^{10}$

Another type of catalyst that has been investigated is the metal-metal oxide (A$\cdot$BO$_x$; A and B are metals) variety. The platinum-tungsten oxide (Pt-WO$_3$) system is one such example that has been studied for electro-oxidation reactions with a potential application as a DMFC catalyst.$^{11}$ In all cases the consensus with respect to fuel cell electro-oxidation catalysts seems to be that the use of multicomponent and multifunctional catalysts is the best strategy for minimizing the noble-metal loading to quantities (µg cm$^{-2}$) that will be cost effective in commercial applications.$^{12}$

The feasibility of employing multicomponent catalysts opens larger composition domains to investigate in an effort to tailor catalysts with specific properties. This in turn results in the inevitable need for high-speed combinatorial methods...
for catalyst discovery to discover and optimize compositions at a rapid pace. Combinatorial discovery methods are now regularly and systematically employed in several fields including drug discovery, optoelectronic materials, and homogeneous and heterogeneous catalysis. With regard to the combinatorial discovery of fuel cell catalysts, synthesis and screening of discrete arrays and continuous gradient libraries have been reported. In this article, we describe an automated system for synthesis and screening diverse combinations of fuel cell catalysts. An integrated, user-friendly, computer-controlled system is reported. Electrolysis is performed using pulsed potential electrodeposition of arrays of catalysts. Following deposition, electrochemical screening experiments are performed in the same setup with minor reconfiguration. The capability of this system towards combinatorial discovery of fuel cell catalysts is demonstrated in a metal-metal oxide fuel cell catalyst library. The Pt-WO3 library is synthesized and screened for methanol electrooxidation activity. Results from physical characterization (i.e., surface structure and composition) and electrochemical characterization experiments are presented.

II. EXPERIMENT

A. Materials

The substrate used for library synthesis was fluorine-doped tin oxide (FTO) on glass (3 in. × 4 in., TEC-15, Hartford Glass Co., Hartford City, IN). The cleaning procedure for the FTO substrate prior to synthesis included sonication in a 1:1 ethanol-water mixture followed by rinsing and further sonication in deionized (DI) water and subsequent drying under a stream of nitrogen.

The precursor salt used for the electrodeposition of Pt was H2PtCl6 (Aldrich) which was dissolved in DI water to the required concentration. A tungsten-peroxo electrolyte was used as the source for the electrodeposition of tungsten-oxide. The tungsten-peroxo electrolyte was prepared by dissolving 1.84 g of tungsten powder (Aldrich) in 60 mL of 30% hydrogen peroxide (Fischer Scientific) solution. The excess peroxide was subsequently decomposed with Pt black. The solution was diluted to 50 mM using a 50:50 mixture of water and isopropanol. The purpose of adding isopropanol is to stabilize the W-peroxo electrolyte and to prevent it from degrading over time. The electrolytes for screening experiments consisted of a combination of sulfuric acid and methanol prepared using DI water and were deaerated using N2 (99.998%, Praxair, Santa Barbara, CA). A RepeaterPro® autopipecer (Eppendorf, Germany) was used to fill in the exact amount of solutions in the electrochemical cells.

B. Automated synthesis and screening system for combinatorial discovery

1. Pulsed electrochemical synthesis

An automated electrochemical synthesis system was developed to create the combinatorial libraries as arrays of different materials. The system consists of three major subsystems: (i) motion subsystem, (ii) computer and software interface and (iii) electrochemical subsystem. Figure 1 shows the block diagram of the setup for automated synthesis and screening. Positioning was achieved using a set of X-Y linear motion stages from NEAT Technologies (Salem, NH) and a VT-80 Z stage from Micos (Germany). The X-stage (Model RM 400) had a range of 400 mm with a maximum velocity of 4 mm s⁻¹, the Y-stage (Model RM 200) had a range of 200 mm with a maximum velocity of 4 mm s⁻¹ and the Z-stage (Model VT-80) had a range of 200 mm with a maximum velocity of 1 mm s⁻¹. The stages were powered by a multistage power amplifier (NuDrive®, National Instruments, Austin, TX) and position control was achieved using a PCI-4X step controller (National Instruments, Austin, TX).

The potential pulse employed during electrodeposition was applied through a potentiostat (Model EG&G 273 A, Princeton Applied Research, Oak Ridge, TN). This was accomplished by driving the potentiostat using a modified software-triggered pulse train (−10 V to +10 V) with a frequency of up to 40 kHz generated with a Data Acquisition Board (DAQ) (PCI-6036E, National Instruments, Austin, TX). The applied voltage and electrochemical current are recorded using an oscilloscope (LeCroy 9361, NY) connected to the potentiostat through analog output ports. The user interface was programmed in LABVIEW® 6i (National Instruments, Austin, TX) where all the aspects of the system, namely, motion control, pulse generation, and data acquisition, are integrated into a user-friendly environment. The user interface can be programmed to any number of samples and geometrical arrays to create libraries of varied sizes with different potential pulse parameters within the limits of the range of the stage travel displacement and the pulse generation system.

The electrochemical hardware consists of two subsystems: (i) a multicell reactor block and (ii) an electrode setup. The substrate (FTO on glass in the present work) is bolted between an aluminum plate and a perforated polypyrrole block (thickness=18 mm). The polypyrrole block consists of a 9 × 7 array of uniformly spaced holes of 6 mm diameter with the center-to-center distance between each hole equal to 10.8 mm. A groove at the bottom of each of the
holes in the polypropylene block hosts an inert O-ring that forms a seal between the substrate and the block, creating an array of independent electrochemical cells.

The reference and counter electrodes are mounted to the X-Y-Z stage using a custom designed HDPE block. A platinum wire wound into a spiral coil was used as the counter electrode and an Ag/AgCl quasi-reference electrode (AgQRE) was used as the reference electrode. The AgQRE wire was wound over the Pt wire with a Teflon™ tape separating the two electrodes providing electrical insulation from each other.

Diverse libraries of materials can be electrosynthesized in an automated fashion using this system. Varying compositions of precursor-metal solutions are filled in each electrochemical cell; the pulse parameters (i.e., upper and lower potentials, pulse frequency, and deposition time), and the array size to be synthesized are entered into the LABVIEW® interface. Executing the application will result in the creation of a diverse catalyst library with varying composition, structure, etc., with minimal or no monitoring during synthesis.

2. High-throughput screening

The electrochemical system was modified for screening by replacing the oscilloscope with a Hewlett-Packard 3440A multimeter interfaced to the computer through the general purpose interface bus (GPIB) port. The potentiostat was controlled through its GPIB interface/computer GPIB card (National Instruments) rather than its analog input/computer data acquisition card. A LABVIEW interface controlled all the systems; the library array size, potential window, potential scan rate, and the number of repeated cyclic voltammograms are user-definable parameters. This program sends commands that call factory-built functions within the potentiostat to create the required linear sweep scans. The cyclic voltammogram measurements are stored in the potentiostat’s memory, which is retrieved by LABVIEW upon completion of each cycle. The potential-current data are automatically saved onto the computer’s hard drive.

3. Library design

A rector block with an \( n \times m \) array of wells is chosen depending upon the number of catalyst compositions one intends to study. A large array would cover a wider composition range; however, with a larger array, a linear increase in the synthesis and screening time is required. In the present work, we chose to investigate a 27-member library with nine different catalyst compositions. Each catalyst was synthesized in triplicate to demonstrate reproducibility.

4. Scanning electron microscopy (SEM)

Structural and compositional analyses of the catalyst samples were performed using SEM and x-ray energy dispersive spectroscopy (EDS). A Philips XL 30 environmental SEM field emission gun electron microscope equipped with a PRISM IG x-ray detector (Princeton Gamma-Tech, Rocky Hill, NJ) was used to carry out electron imaging and quantitative compositional analysis. An accelerating voltage of 10 kV was used in all the SEM-EDS experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Array elements</th>
<th>Volume of 5 mM ( \text{H}_2\text{PtCl}_6 ) (mL)</th>
<th>Volume of 50 mM W-peroxo electrolyte (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>[1,1], [1,2], [1,3]</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>S2</td>
<td>[1,4], [1,5], [1,6]</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>S3</td>
<td>[1,7], [1,8], [1,9]</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>S4</td>
<td>[2,1], [2,2], [2,3]</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td>S5</td>
<td>[2,4], [2,5], [2,6]</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>S6</td>
<td>[2,7], [2,8], [2,9]</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>S7</td>
<td>[3,1], [3,2], [3,3]</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>S8</td>
<td>[3,4], [3,5], [3,6]</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>S9</td>
<td>[3,7], [3,8], [3,9]</td>
<td>1.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSION

A \( 3 \times 9 \) array of Pt-WO\(_3\) library was synthesized using the automated pulsed-potential electrochemical synthesis routine. The compositional variation was achieved by varying the amounts of \( \text{H}_2\text{PtCl}_6 \) and W-peroxo electrolyte in the deposition solution. Table I shows the compositions of the solutions and the corresponding sample numbers in the catalyst array; nine different solution compositions were used and each composition was prepared in triplicate. Library synthesis consisted of immersing the electrode probe (consisting of the counter and reference electrodes) into each of the electrolyte-filled reactor cells and applying a square-wave potential pulse between \(-1.5\) V and \(0\) V versus AgQRE at a frequency of 200 Hz for 5 min. As described in the experimental section, the entire process was automated through computer control allowing unattended operation. After the synthesis of the Pt-WO\(_3\) catalyst library the reaction wells were emptied of the electrolyte and cleaned thoroughly with DI water. Subsequent electrochemical screening was performed in sulfuric acid and methanol.

Surface structural and compositional analysis was performed following the electrochemical screening experiments. Figure 2 shows the SEM micrographs of representative samples in the catalyst array. Sample S1 (pure Pt) consisted of spherical Pt particles with a wide range of particle size distribution [Fig. 2(a)]. The particle sizes ranged from a few tens of nanometers to around 200 nm. Figure 2(b) shows a representative SEM micrograph of the Pt-WO\(_3\) region. Note that samples containing WO\(_3\) (samples S2 through S9) exhibit larger particle sizes (compared to pure Pt) and tend to form aggregates of near uniformly sized particles. The heterogeneous particles were observed to agglomerate significantly more than the pure Pt particles which typically consisted of isolated clusters.

The relative compositions of Pt and W in the Pt-WO\(_3\) catalysts were measured using x-ray energy dispersive spectroscopy. Figure 3 shows the composition of tungsten (at. %) as a function of the tungsten concentration (mol %) in the deposition solution. As expected, the composition of tungsten increases with the increase in the amount of tungsten in solution, with the maximum composition of tungsten obtained in this study at \(\approx 25\%\). This can be increased to a higher value by using a higher concentration of W-peroxo...
electrolyte and a lower concentration of $\text{H}_2\text{PtCl}_6$. Nevertheless, the present work demonstrates the ability to create multicomponent catalyst libraries in an automated fashion through pulsed electrochemical deposition.

In order to determine the chemical state of the Pt-WO$_3$ materials, x-ray photoelectron spectroscopy was employed. Measurements (data not shown here) reveal the valence of Pt as Pt$^0$ and W as W$^{6+}$, which corresponds to WO$_3$. This indicates that Pt and W do not form an alloy; rather, metallic Pt is dispersed within a WO$_3$ matrix. X-ray diffraction measurements determined that the films are amorphous (data not shown) as no heat treatments were employed after electrochemical deposition.

The electrochemical activity of the Pt-WO$_3$ catalyst library was screened in sulfuric acid and methanol solutions. Figure 4 shows the results of cyclic voltammograms obtained at each of the catalyst spots in a 0.5 M $\text{H}_2\text{SO}_4$ solution. The potential was cycled until a stable voltammogram is obtained; typically ten cycles were performed on each of the catalyst compositions in the library. From Fig. 4, the sample S1 exhibits the typical behavior of a polycrystalline Pt. Two characteristic peaks and a broad background current in the region $-0.55$ to $-0.2$ V versus AgQRE reflect the hydrogen underpotential deposition (H-UPD) and corresponding desorption that occurs on the various planes [namely, (100), (110), and (111)] in the polycrystalline Pt.$^{19}$ As we move along the samples in the Pt-WO$_3$ library, changes in the H-UPD region of Pt can be noticed, evidently, due to the presence of WO$_3$. The H-UPD peaks appear broader as the W composition increases. It is well-known that WO$_3$ can intercalate hydrogen in the potential region of $-0.55$ to $-0.1$ V. Therefore, the Faradaic current exhibited in the Pt-WO$_3$ catalysts in the aforementioned potential is the summation of the contributions from both Pt and WO$_3$ components of the catalyst. From Fig. 4, it can also be noted that the magnitude of the currents decrease with the increase of WO$_3$. This might be due to the result of a lower amount of the catalyst deposited as the amount of W increases. This can be explained considering the fact that the deposition rate of WO$_3$ is much lower compared to that of Pt and that in our study we held the deposition time of each catalyst constant (5 min).

The electrocatalytic activity of the Pt-WO$_3$ library was tested in a solution containing 0.5 methanol/0.5 M $\text{H}_2\text{SO}_4$ (Fig. 5). The pure Pt sample (S1) exhibits the expected behavior of a polycrystalline Pt electrode. The H-UPD peaks are suppressed which is evident from the low currents in this region. This is due to the fact that methanol adsorbs on Pt sites at these potentials resulting in a decrease in the number of sites available for underpotential deposition of hydrogen. As the potential is increase to higher values, methanol oxi-
the catalysts. In fact, Pt-WO$_3$ compared to sample S1 oxidation currents are noticed. This is due to the fact that a catalyst composition can be combined with EDS data to identify the highly active catalysts. This is demonstrated during the electrochemical screening stage. This means the highest current density at the lowest potential can be identified using the automated synthesis and screening procedure outlined in this study can be extended to other electrocatalytic systems, for example, electrocatalysts for oxygen reduction.

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