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# Combinatorial electrochemical cell array for high throughput screening of micro-fuel-cells and metal/air batteries

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An electrochemical cell array was designed that contains a common air electrode and 16 microanodes for high throughput screening of both fuel cells (based on polymer electrolyte membrane) and metal/air batteries (based on liquid electrolyte). Electrode materials can easily be coated on the anodes of the electrochemical cell array and screened by switching a graphite probe from one cell to the others. The electrochemical cell array was used to study direct methanol fuel cells (DMFCs), including high throughput screening of electrode catalysts and determination of optimum operating conditions. For screening of DMFCs, there is about 6% relative standard deviation (percentage of standard deviation versus mean value) for discharge current from 10 to 20 mA/cm<sup>2</sup>. The electrochemical cell array was also used to study tin/air batteries. The effect of Cu content in the anode electrode on the discharge performance of the tin/air battery was investigated. The relative standard deviations for screening of metal/air battery (based on zinc/air) are 2.4%, 3.6%, and 5.1% for discharge current at 50, 100, and 150 mA/cm<sup>2</sup>, respectively. © 2007 American Institute of Physics. [DOI: 10.1063/1.2755439]

## I. INTRODUCTION

With increasing demands on the diversity of functional materials in modern science and technology, the combinatorial method has received much attention since the middle of the 1990s,<sup>1,2</sup> with which a number of parallel material samples are studied at the same time. A variety of instruments and methods have been used for generating combinatorial libraries and screening of material samples, including fluorescence spectroscopy,<sup>3</sup> sensors,<sup>4,5</sup> mass spectroscopy,<sup>6,7</sup> high performance liquid chromatography (HPLC)/mass spectroscopy,<sup>8</sup> and Fourier transform infrared (FTIR) and FT Raman methods.<sup>9</sup> The first application of the combinatorial method in electrochemical research<sup>2</sup> was reported in 1998 when Reddington *et al.* employed an optical method for the screening of electrocatalysts. Thereafter, the combinatorial electrochemical method has played an important role in the discovery of novel catalysts for fuel cells<sup>10–21</sup> and functional materials for batteries.<sup>22,23</sup> An increasing number of instruments and methods have been developed for combinatorial electrochemical research. Strasser *et al.*<sup>24</sup> used a sputter technique to deposit thin films of electrocatalysts for building an electrode array. Sullivan *et al.*<sup>25</sup> developed a computer-automated device for quantitatively measuring the electrochemical current of a 64-member electrode array. Kulikov *et al.*<sup>26</sup> reported an automated system for the quantitative synthesis and screening of conductive polymers. Guerin *et al.*<sup>15</sup> developed hardware and software for automatically measuring a 64-member electrochemical array. Recently, several complex robotic systems<sup>27–30</sup> were reported for combinatorial electrochemical synthesis and measurement. These automated methods need complex combinatorial cell design, multiple printed electric leads, special equipment, computer

software, and long term engineering work, which may significantly decrease the benefit offered by the combinatorial method.

In order to facilitate our research and development on fuel cells and metal/air batteries, we have developed a series of relatively simple combinatorial methods,<sup>31–34</sup> which do not need special electrochemical equipment. High throughput screening of electrode materials and evaluation of fuel cells can be carried out with these simple methods. For example, a movable electrolyte probe<sup>31</sup> for screening anode catalysts of direct methanol fuel cell (DMFC) and an electrode/electrolyte probe<sup>34</sup> for screening anode materials of metal/air battery were developed in our laboratory. Unfortunately, the methods described previously can only use water-based electrolytes such as KOH and H<sub>2</sub>SO<sub>4</sub>. In the present research, we will demonstrate a combinatorial cell array that is suitable for both electrochemical systems using water-based electrolytes and polymer electrolyte membranes. Micro-membrane-electrode-assemblies (MEAs) for fuel cells can be formed; and micro-metal/air-batteries can be generated on a small area of the combinatorial electrochemical cell array. A chemically inert and electrically conductive rod can be used for a general screening probe. The only difference between the two systems is that the cell array for fuel cells uses a polymer electrolyte membrane and, for metal/air batteries, it uses a hydrophilic microporous separator.

## II. METHOD AND EXPERIMENTAL PROCEDURES

### A. Design of electrochemical cell array

A 16-member electrochemical cell array was designed, which consists of two parts: a common air-electrode part on the bottom and an anode-array part on the top. As shown in

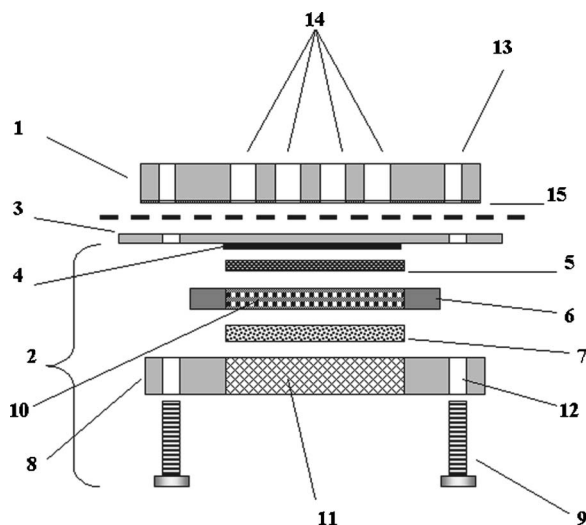


FIG. 1. A longitudinal cross-section view of a disassembled combinatorial electrochemical cell array. 1, top anode end-plate with 16 cylindrical holes for anode material coating and screening; 2, components of air electrode on lower part of the cell array; 3, electrolyte membrane (or battery separator); 4, platinum catalyst coating for catalytic oxygen reduction; 5, carbon cloth for gas diffusion electrode; 6, cathode current collector with small holes for air passage; 7, air filter; 8, bottom cathode end plate with small holes for air passage; 9, bolt for assembling; 10, area for air passing on the cathode current collector; 11, area for air passing on cathode end plate; 12, hole for inserting bolt on cathode end plate; 13, hole for inserting bolt on anode end plate; 14, holes for anode material coating and screening; and 15, Teflon gasket for the electrode array on the bottom of the anode end plate.

Fig. 1, a dashed line is used to separate the anode-array part and the common air-electrode part. The area of the whole cell array is  $6.0 \times 6.0 \text{ cm}^2$ , on which the 16-member anode array takes  $3.5 \times 3.5 \text{ cm}^2$ . The common air-electrode supplies air to the cathodes of the cell array and catalyzes oxygen reduction by air convection, which consists of six layers. From the top to the bottom of the air electrode, there is a polymer electrolyte membrane layer,  $250 \text{ }\mu\text{m}$  thick (or a battery separator layer,  $150 \text{ }\mu\text{m}$  thick), a cathode catalyst layer ( $10\text{--}15 \text{ }\mu\text{m}$  thick), a gas diffusion layer ( $450 \text{ }\mu\text{m}$ ), a cathode current collector layer ( $1.1 \text{ mm}$  thick), an air filter layer ( $2.0 \text{ mm}$  thick), and a cathode end-plate layer ( $8.5 \text{ mm}$  thick). For fuel cell research, Nafion 117 (purchased from Dupont) was used as the electrolyte membrane. For metal/air battery research, microporous polyestersulfone film was used as the separator. The gas diffusion layer was carbon cloth (purchased from E-Tek). A titanium sheet with small holes was used as the cathode current collector, which is inert to chemical and electrochemical reactions. The cathode end plate was made of a plate of organic glass that was processed with small holes on the center for air passage. The cathode catalyst was platinum black (purchased from Johnson Matthey). The total thickness of the cathode part was  $12.5 \text{ mm}$ .

The top anode-array part of the electrochemical cell array is relatively simple with only two layers. The main layer was made of a plate of organic glass ( $8.5 \text{ mm}$  thick), which was covered by a Teflon gasket ( $200 \text{ }\mu\text{m}$  thick) on its bottom face in order to obtain the best sealing between the anode and cathode parts. Figure 2 shows an overperspective view of the combinatorial electrochemical cell array with 16 holes for coating and screening of anode electrode materials. The top

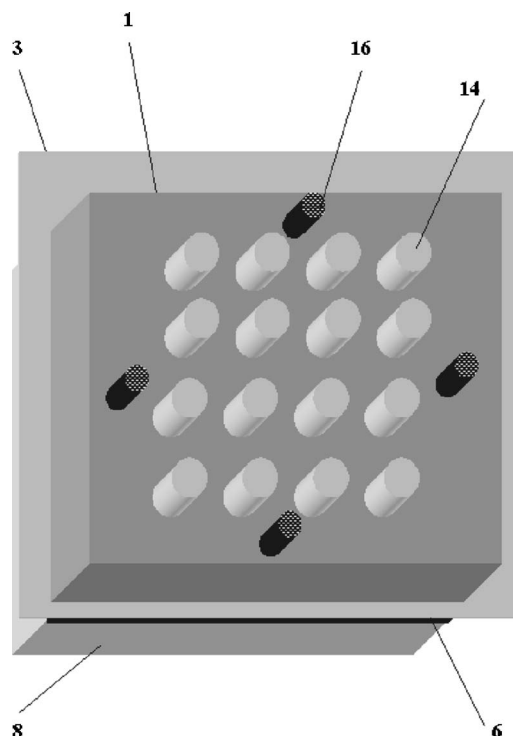


FIG. 2. An overperspective view of a combinatorial electrochemical cell array with 16 holes for coating and screening of anode electrode materials. 16, bolt area. The labels 1, 3, 6, 8, and 14 have the same meanings as described in Fig. 1.

anode cell-array part and the bottom common air-electrode part were tightly jointed together with four bolts. Samples of anode electrode materials can be filled in the cylindrical holes and coated on the surfaces of the electrolyte membrane or the battery separator. The electrode area of each cell in the cell array was  $0.2 \text{ cm}^2$ . For MEA experiments, a 5% Nafion solution (purchased from Aldrich Chemical Co.) was used as the binder. For metal/air battery experiments, the metal powders can be tightly deposited on the surface of the separator with a few drops of KOH solution.

## B. MEA experiments for research on direct methanol fuel cells (DMFCs)

Nafion 117 membrane was treated with 3%  $\text{H}_2\text{O}_2$  under warm conditions ( $70\text{--}80 \text{ }^\circ\text{C}$ ) for 2 h. After a full washing to remove the residual  $\text{H}_2\text{O}_2$ , it was continuously treated with  $1\text{M}$   $\text{H}_2\text{SO}_4$  under mild boiling conditions for 2 h. Then, it was fully washed with de-ionized water. A piece of treated Nafion 117 membrane ( $6 \times 6 \text{ cm}^2$ ) was taken and dried on a gel drier for about 40 min for preparation of micro-MEAs. An emulsion of Pt ink was made with Pt black, Nafion solution (5% product from Aldrich Chemical Co.), and water by ultrasonication. The Pt ink was coated on a  $3.5 \times 3.5 \text{ cm}^2$  carbon cloth and dried to remove the residual solvents. The final dry catalyst material on the carbon cloth contained 93% Pt black and 7% pure Nafion. The carbon cloth coated with catalyst and the Nafion 117 membrane after treatment and drying were hot pressed at  $125 \text{ }^\circ\text{C}$  under 1500 psi pressure for 2 min. The resulting combination of Nafion 117 membrane, Pt catalyst coating, and carbon cloth formed the main part of the common air-electrode side, which was assembled

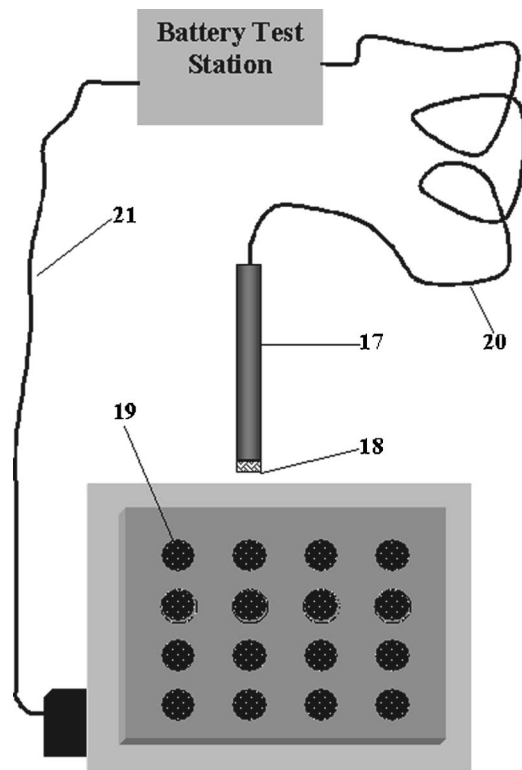


FIG. 3. A perspective view of an electrochemical system using a combinatorial cell array for high throughput coating and screening of electrode materials. 17, graphite rod as a screening probe; 18, hydrophilic carbon paper for fuel and electrolyte diffusion; 19, anode coating; 20, lead for communicating between a battery test station and the electrochemical cells in the cell array; and 21, lead for communicating between a battery test station and the common cathode of the cell array.

into a combinatorial electrochemical cell array in the method as described in Fig. 1. The processing of anode ink is similar to that of cathode ink, except for the use of PtRu alloy powder (or Pt and Ru metal mixture) to replace the Pt. The anode ink was injected into the holes of the top anode plate (see Fig. 2) with a microsyringe, which formed a coating on the surface of the Nafion 117 membrane with an area of 0.2 cm<sup>2</sup> for each cell. A 0.17 cm<sup>2</sup> piece of hydrophilic carbon paper was covered on the top of the anode catalyst surface for each electrode. After coating, the combinatorial electrochemical cell array was dried to remove solvents in the anode ink at 70 °C for 1 or 2 h. The final dry catalyst material of the anode contained 85% PtRu and 15% dry Nafion. After being cooled to room temperature, three drops (ca. 0.2 ml) of methanol solution with a specified concentration were filled into each of the holes on the anode plate of the cell array, where methanol was the fuel. At the cathode, the oxygen was provided by the ambient air. These micro-DMFC cells were conveniently screened with a graphite rod (ca. 0.17 cm<sup>2</sup>). Figure 3 shows a method of electrical connections among the electrochemical cell array, the screening probe, and the battery test station for carrying out high throughput measurements of these micro-fuel-cells. After completing one measurement on one cell, the graphite rod was switched into the other holes on the cell array until all of the cells were screened. About a few minutes are needed for screening one cell and obtaining a full voltage-current curve. All the elec-

trochemical experiments were carried out at room temperature (ca. 20 °C).

### C. Experimental procedures for metal/air batteries

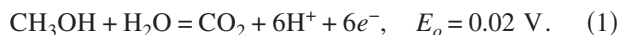
A 6 × 6 cm<sup>2</sup> piece of hydrophilic microporous polyester-sulfone film with a pore size of 0.45 μm was used as the separator. The Pt ink was coated on the carbon cloth in the same method as described above for the micro-MEA experiments. There was no hot pressing between the carbon cloth and the separator. After assembling the cell array, a sample of 50 mg zinc power (or 100 mg tin powder) was filled into each hole on the anode plate of the cell array, on which a hydrophilic carbon paper (ca. 0.19 cm<sup>2</sup>) was covered. Then, three drops of 50% KOH were filled into each hole before the electrochemical measurements, where metal powder was the fuel; and air from the ambient was oxidant. For tin/air battery experiments, a small amount of Cu(NO<sub>3</sub>)·2H<sub>2</sub>O salt was added into the tin powder to improve the electrical conductivity among the tiny metal powders of the anode electrodes. All the electrochemical experiments were carried out at room temperature (ca. 20 °C).

## III. RESULTS AND DISCUSSION

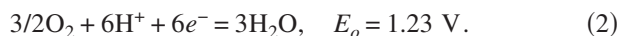
### A. Electrochemical systems with polymer electrolyte membrane

In a practical DMFC, a polymer electrolyte membrane is used as the electrolyte for separating the anode and the cathode. The electrode reactions of a DMFC are as follows:

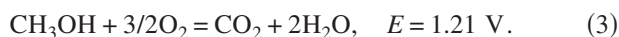
At the anode,



At the cathode,



The overall cell reaction is



The theoretical cell voltage of a DMFC is 1.21 V. Practically, the open circuit voltage of a DMFC (ca. 0.7 V) is far below the theoretical value because of slow electrode kinetics for methanol oxidation at the anode and oxygen reduction at the cathode, which is one of the main challenges of the DMFC. The secondary main challenge is methanol crossover from the anode to the cathode through the electrolyte membrane, which contaminates the cathode catalyst and further decreases the cell voltage. Innumerable experiments are needed to study potential electrode catalysts, novel electrolyte membranes, and optimum operating conditions in order to overcome the main challenges since there is much interest in DMFC due to its high theoretical energy density (6100 Wh/Kg). Combinatorial method is a smart way to facilitate the research and development of DMFCs.

### 1. Experimental deviation of screening micro-DMFCs

An electrochemical cell array containing 16 micro-DMFCs was formed under parallel experimental conditions in order to examine the experimental deviation. Figure 4 shows the voltage-current curves of the 16 DMFCs using 2.5M methanol as fuel. From the voltage-current curves ob-



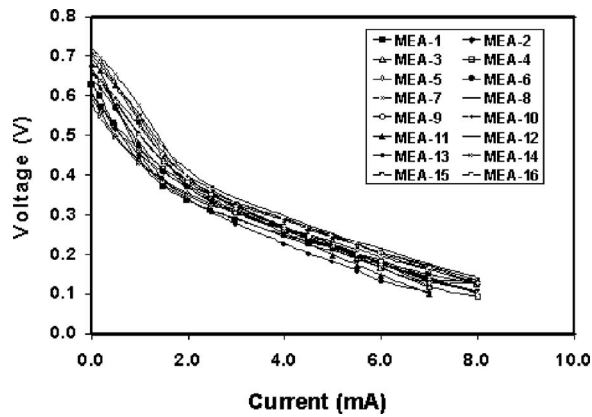


FIG. 4. Voltage-current curves of 16 parallel direct methanol micro-fuel-cells measured with a combinatorial electrochemical cell array.

tained from different cells, it is apparent that the voltages at different discharge currents are not identical even if the operating conditions are the same. There are experimental deviations among these measurements. The open circuit voltage fluctuates between 0.58 and 0.72 V around a mean value of 0.65 V. There is a maximum deviation of 0.070 V and a standard deviation of 0.042 V at open circuit (or zero discharge current). The standard deviations at other discharge currents are also listed in Table I. The open circuit voltage has the highest standard deviation due to the highest methanol crossover rate that interferes with the accuracy of the electrochemical measurements. The average standard deviation for other discharge currents is about 20 mV, and the percentage of standard deviation versus mean value is about 6%. The experimental accuracy allows the electrochemical cell array to be useful for research on fuel cells.

2. Effect of methanol concentration on discharge performance of micro-DMFCs

The effect of methanol concentration on the discharge performance of micro-DMFCs was studied. Figure 5 shows voltage-current curves of DMFCs under various methanol concentrations obtained with the electrochemical cell array. The open circuit voltage significantly increases with methanol concentration from 0.2M to 0.5M and then has almost no apparent change from 0.5M to 1.5M. The low cell voltage at 0.2M methanol can be explained by the thermodynamics of the methanol/air cell as described by the Nernst equation {according to Eq. (3),  $E=E_o-(RT/1.5F)\ln[P_{CO_2}/(C_{MeOH}P_{O_2}^{3/2})]$ , where  $E_o$  is the cell potential at a standard condition}. The potential of the methanol/air cell depends on both the concentrations of oxidant at the cathode and reductant at the anode, where they are separated by a polymer electrolyte membrane. However, continuing to increase the methanol concentration from

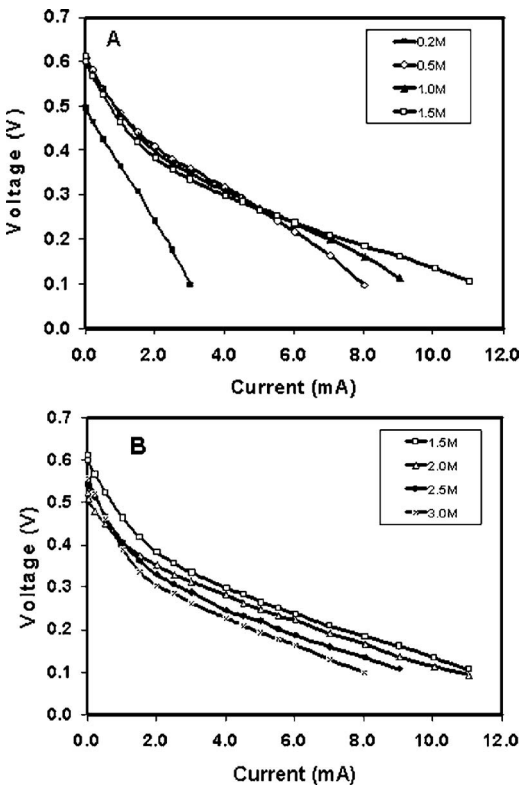


FIG. 5. Effect of methanol concentration on the behaviors of voltage-current curves for micro-methanol/air-fuel-cells in a combinatorial electrochemical cell array. (A) The cell's performance increases with increasing methanol concentration from 0.2M to 1.5M; and (B) the cell's performance decreases with increasing methanol concentration from 1.5M to 3.0M.

1.5M to 3.0M decreases the open circuit voltage slowly instead of increasing it. The decrease of the open circuit voltage with methanol concentration is attributed to increased methanol crossover at higher methanol concentration, which contaminates the cathode catalyst and causes the cathode voltage to decrease. Methanol mass transfer controls the increase of the discharge current for methanol concentrations from 0.2M to 1.5M. At 0.2M methanol, the amount of fuel being supplied is not enough to maintain the discharge current. The mass transfer limitation is more apparent at the higher current range on the voltage-current curves. However, continuing to increase the methanol concentration from 1.5M to 3.0M decreases the discharge current instead of increasing it, which is attributed to methanol crossover that lowers the cathode voltage and in turn the total cell voltage. The experimental results obtained with the electrochemical cell array are consistent with those of traditional DMFCs.<sup>35</sup>

3. Effect of mixed metal catalysts on discharge performance of micro-DMFCs

The effect of mixed metal catalysts on the discharge performance of micro-DMFCs was studied with the electrochemical cell array. It is well known that PtRu binary metal alloy<sup>36</sup> can significantly overcome the anode poisoning of DMFC caused by the formation of an intermediate CO in methanol oxidation on the Pt catalyst surface. We have tried to use mixed Pt and Ru metals, instead of PtRu alloy, as the anode catalyst of micro-DMFCs to study if a similar catalytic activity exists. Figure 6 shows voltage-current curves of

TABLE I. Standard deviations obtained from 16 samples of micro-DMFCs.

Current (mA)	0.0	2.0	3.0	4.0
Mean value (V)	0.655	0.372	0.312	0.266
Standard deviation (V)	0.042	0.024	0.017	0.018
% standard deviation vs mean	6.4	6.4	5.5	6.9

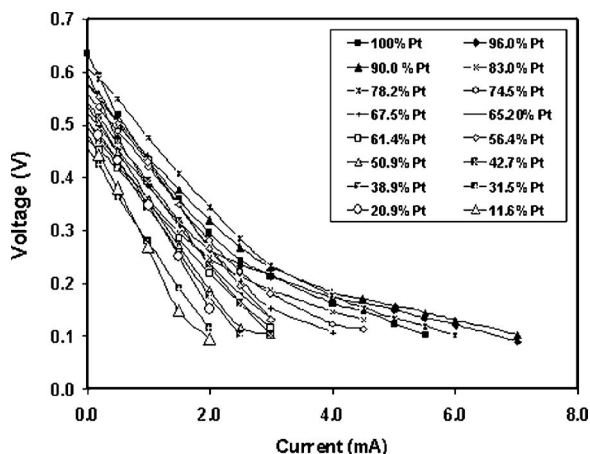


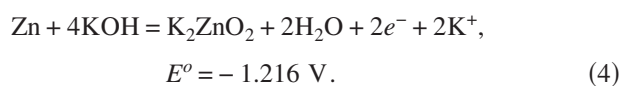
FIG. 6. Voltage-current curves of direct methanol micro-fuel-cells using mixed Pt and Ru blacks as the anode catalysts. The results were obtained with a combinatorial electrochemical cell array. Methanol concentration: 2.5M.

micro-DMFCs obtained with the electrochemical cell array. The discharge performances among these curves can be compared by looking at the voltages at the same current value. At 78% Pt content, we obtained the highest voltages for the current range between 0.2 and 3.0 mA. The overall performance decreases if the Pt content is lower or higher than 78%. The catalytic activity using mixed Pt and Ru metals as the anode catalyst of DMFC is apparently different from that of using PtRu alloy.<sup>36–38</sup> According to the mechanism of catalytic oxidation of methanol, the pure Pt active sites can catalyze methanol molecules to quickly remove four electrons and four protons and form a Pt–CO intermediate adsorption complex. The further removal of two electrons and two protons needs to add a water molecule and form CO<sub>2</sub>. Because it is very slow for Pt to hydrate and dissociate the CO intermediate, the Pt catalytic sites are poisoned. On the other hand, the pure Ru catalytic sites can easily activate a water molecule and remove a proton and an electron to form a Ru–OH intermediate adsorption complex but cannot catalyze methanol molecules to further remove protons and electrons, which results in no catalytic activity to methanol oxidation. However, the combination of Pt and Ru (or PtRu alloy) can catalyze methanol oxidation much faster because the combination of the intermediates of Ru–OH and Pt–CO can very easily remove the last electron and proton to form a CO<sub>2</sub>. As the mixed Pt and Ru metals can only form a small amount of such combinations of Ru–OH and Pt–CO as compared with the PtRu alloy, its overall catalytic activity is apparently lower than that of the PtRu alloy.

## B. Electrochemical systems with liquid electrolyte

Many electrochemical systems use liquid electrolytes, such as zinc/air or tin/air batteries. For a zinc/air battery, the electrode reactions are as follows:

At the anode,



At the cathode,

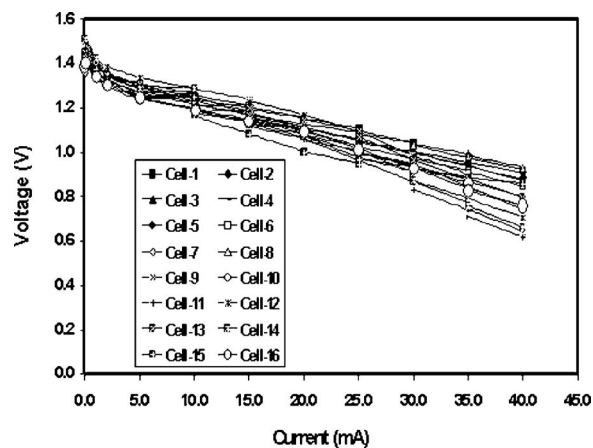
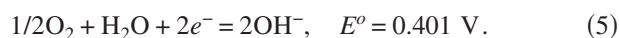
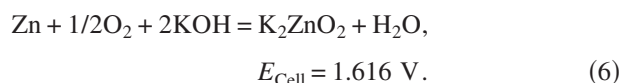


FIG. 7. Voltage-current curves of micro-zinc/air-batteries obtained with a combinatorial electrochemical cell array.



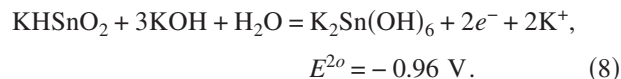
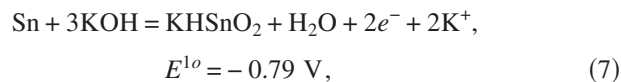
The overall cell reaction is



The theoretical cell voltage is 1.62 V.

For tin/air battery the electrode reactions are as follows:

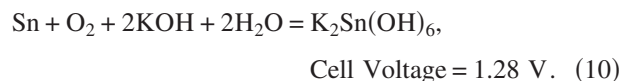
At the anode,



At the cathode,



The overall cell reaction is the four-electron oxidation of Sn,



The theoretical cell voltage is 1.28 V.

## 1. Experimental deviation of screening micro-zinc/air-batteries

An electrochemical cell array containing 16 micro-zinc/air-batteries was formed under parallel experimental conditions in order to examine the experimental deviation. Figure 7 shows voltage-current curves of 16 micro-zinc/air-batteries. From the voltage-current curves obtained from different cells, it is apparent that the voltages at different discharge currents are not identical even if the operating conditions are the same. There are experimental deviations among these measurements. The open circuit voltage fluctuates between 1.36 and 1.51 V around the mean value of 1.43 V. There is a maximum deviation of 0.080 V and a standard deviation of 0.043 V at open circuit (or zero discharge current). The standard deviations at other discharge currents are listed in Table II. The standard deviation increases with increasing discharge current except at open cir-

TABLE II. Standard deviation obtained from 16 samples of micro-zinc/air-batteries.

Current (mA)	0	10	20	30
Mean value (V)	1.431	1.238	1.098	0.958
Standard deviation (V)	0.043	0.030	0.039	0.049
% deviation vs mean	3.0	2.4	3.6	5.1

cuit voltage. Compared with the data of DMFCs that use polymer electrolyte membranes, the zinc/air batteries that use water-based electrolyte have much higher voltage and discharge currents. It is noticeable that the zinc/air batteries have much smaller relative standard deviations (i.e., standard deviation versus mean value) than those of the DMFCs, which is attributed to the higher ionic conductivity of the water-based electrolyte than that of the polymer electrolyte.

2. Effect of Cu content in the anode electrode on the discharge performance of tin/air battery

We have further tested the electrochemical cell array for its application in a water-based electrolyte system. The effect of Cu content in the anodes on the discharge performance of tin/air batteries was studied. Here, we did not add Cu metal directly. We added Cu salt into the anode, which was reduced to Cu metal at the anode when it contacted with the tin powders. Figure 8 shows voltage-current curves of a number of micro-tin/air-batteries, in which there are different contents of Cu salt in the anode electrodes. As the Cu salt in the

TABLE III. Effect of Cu-salt content in the anode electrode on the discharge current of micro-tin/air-batteries.

Voltage (V)	Discharge current (mA)			
	Cu-salt content			
	0%	5%	10%	15%
0.80	4.0	7.0	9.0	45.0
0.70	5.0	10.0	15.0	57.5
0.60	8.0	13.0	21.0	63.0

anodes was quickly reduced to Cu metal and coated on the tin particles' surfaces, the electrical conductivity of the anode is significantly improved. The discharge performance increases significantly with increasing percentage of Cu salt until it reaches 15%. As compared with the pure tin anode (0% Cu salt) for the tin/air batteries, the discharge current at 15% Cu salt increased about eight to ten times. Table III summarizes the variation of discharge current of tin/air batteries with different Cu-salt contents and discharge voltages. However, further increasing the content of Cu salt over 15% will gradually decrease the discharge performance as the tin content is significantly diluted by the addition of Cu salt in the anode of the tin/air batteries.

In summary, an electrochemical cell array was designed that contains a common air electrode and 16 microanodes for high throughput screening of fuel cells and metal/air batteries. For fuel cell application, the electrochemical cell array uses polymer electrolyte membrane as electrolyte. As demonstrated, 16 parallel samples of anode catalysts can be simultaneously coated on the Nafion 117 membrane in the electrochemical cell array to form 16 micro-DMFC single cells. The average of standard deviation is 20 mV, and the percentage of standard deviation versus mean value is 6%. The effect of methanol concentration on the DMFCs' performance was studied. The discharge performance increases for methanol concentration from 0.2M to 1.5M and then decreases for methanol concentration from 1.5M to 3.0M. The result is consistent with those of traditional DMFC experiments. The electrochemical cell array was also used to study binary metal catalysts using mixed Pt and Ru for DMFCs. At 78% Pt content, the highest catalytic activity was obtained for the current range between 0.2 and 3.0 mA (or between 1 and 15 mA/cm<sup>2</sup>).

For metal/air battery application, the electrochemical cell array used a hydrophilic microporous polyestersulfone film as the separator. The standard deviation was examined using 16 parallel samples of zinc/air battery, which increases with increasing discharge current. For currents at 10, 20, and 30 mA (or 50, 100, and 150 mA/cm<sup>2</sup>), the standard deviations are 30, 39, and 49 mV, or the percentage of standard deviation versus mean value are 2.4%, 3.6%, and 5.1%, respectively. The electrochemical cell array was used to study the effect of the addition of Cu salt in the anode electrode on the discharge performance of micro tin/air batteries. As compared with the pure tin anode (0% Cu salt) for the tin/air batteries, the discharge current at 15% Cu salt increases about eight to ten times.

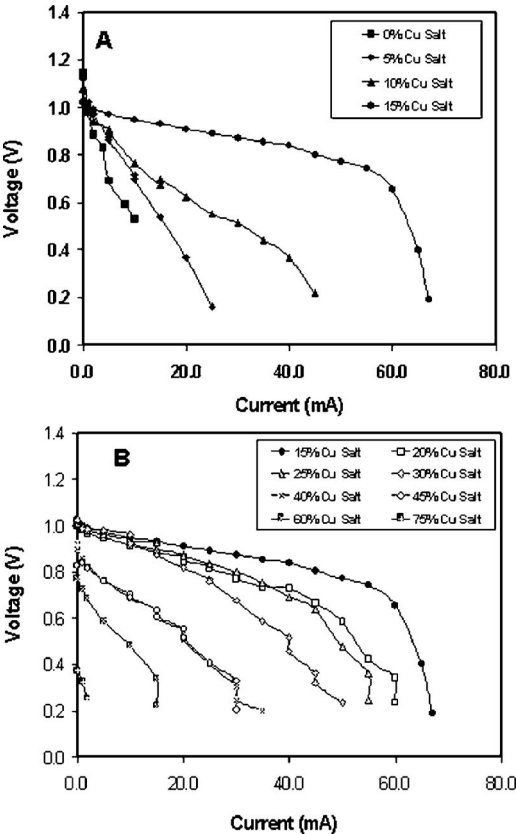


FIG. 8. Effect of addition of Cu salt into the anode on micro-tin/air-batteries. The results were obtained with a combinatorial cell array. (A) The cell's performance increases with increasing Cu salt from 0% to 15%; and (B) the performance decreases with increasing Cu salt from 15% to 75%.

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