

# An innovative process for PEMFC electrodes using the expansion of Nafion film

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## Abstract

Swelling of a Nafion film makes it very difficult to deposit thin catalyst layers on a membrane electrolyte. In this study, a process has been developed that utilizes the expansion of Nafion film in the deposition so as to mitigate this problem. When the film is fully expanded, catalyst ink can be applied on to the membrane directly by means of spraying or blade pasting without concerns over swelling. The resulting membrane electrode assembly shows good performance relative to commercial products.

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*Keywords:* Proton exchange membrane fuel cell; Catalyst layer; Swelling; Nafion film; Gas-diffusion electrode

## 1. Introduction

Increase in the utilization of catalyst is always a significant factor to lower material costs for proton exchange membrane fuel cells (PEMFCs) without sacrificing performance and reliability. One of the most significant improvements has been to impregnate the catalyst layers of PTFE-bound gas-diffusion electrodes with solubilized ionomer [1]. The catalyst utilization is still, however, only about 10–20% [2]. To achieve higher catalyst utilization, an alternative fabrication method for the membrane electrode assembly (MEA) was proposed [3,4], by which ionomer was used as the binding agent without PTFE in the ink preparation, and the ink was applied directly on to the membrane rather than on the gas-diffusion layer. The thin-film catalyst layer maintained intimate contact with the ionomer, which improved not only the catalyst utilization but also the continuity of the catalyst layer/membrane interface. The key technique in that work was to let a vacuum table hold the membrane in place, and then apply catalyst ink on the membrane to avoid the loss of dimensional control that would otherwise be caused by membrane swelling. After ink drying and formation of the catalyst layer by heating, the process was repeated on the other side of the membrane. Vacuum tables are not ideal for low cost, mass production processes. The two steps of MEA fabrication may harm the

catalyst structure or cause loss of dimensional control on one side of MEA due to too strong vacuum while forming the catalyst layer on the other side or to membrane swelling in the absence of sufficient holding forces. Based on the thin-film concept, Hulett [5] proposed an alternative MEA process in which the membrane was pre-swollen before the catalyst ink was applied. After applying ink, the membrane with ink was prevented from shrinking in the  $x$ - $y$  dissections during drying. Although the employment of a pre-swollen membrane did overcome the swelling problem, the membrane was not fully expanded and the degree of swelling was only partially reduced. In addition, the constraint during drying would change the membrane's properties, such as original dimensions, water adsorption, and ion conductivities.

The object of the present study is to design a new method for manufacturing the MEA that can overcome the problem of deforming when coating the catalyst ink on the electrolyte membrane. To alleviate the swelling, the membrane is pre-expanded by solvent treatment. A certain time is required for the full expansion of the membrane. Thereafter, deforming does not occur when the ink is applied on the membrane surface. This allows the catalyst to be applied to both side of membrane either simultaneously or in a sequential manner before the drying process. The two catalyst layers are then dried slowly to achieve even shrinkage of electrolyte membrane, which results in intimate contact between the catalyst and the ionomer. The drying temperature is then raised to the final curing temperature to complete the process.

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The expansion method with a proper drying procedure can make the catalyst structure fine and delicate. The benefit of the method is that it can be easily conducted without the need of sophisticated apparatus.

## 2. Experimental

The degree of membrane expansion under different solvent treatments was first examined. The purpose was to decide which solvent caused the largest expansion:shrinkage ratio before the catalyst-deposition step, since the less the shrinkage, the less would be the deformation. Water, ethylene glycol (EG) and glycerol were selected as solvents. The expansion:shrinkage ratios in three directions ( $x$ -direction is the membrane manufacture direction,  $y$ -direction is the transverse direction, and  $z$ -direction is the thickness) were measured after an adequate period. The expansion measurements were taken with the membrane immersed in the solvent and the shrinkages were measured in open air. Nafion 117 ( $H^+$  form, EW 1100, 7 mil, DuPont) was used in all experiments. The membranes were first treated in a 3 wt.%  $H_2O_2$  at  $70^\circ C$  for 1 h and thoroughly washed four to five times with DI water in an ultrasonic bath. The membranes were then kept in 0.5 M  $H_2SO_4$  at  $70^\circ C$  for 1 h and washed again with deionized water (four to five times) in an ultrasonic bath. The clean membranes were then dried and stored before use.

The flow sheet of the proposed process is shown in Fig. 1. EG was chosen to be the expansion agent for the membrane and EG was also used as the dispersion agent in preparing the catalyst ink. The ink was composed of Pt/C powder (20 wt.% Pt, E-TEK), Nafion solution (5 wt.%, Aldrich) and EG. The finely ground Pt/C powder was first mixed with EG, and then Nafion solution was slowly added with stirring. Finally, the mixture was agitated by means of ultrasonic waves (Sonicator XL-2020, Heat Systems Inc.). The formula ratios of the Pt/C powder, Nafion solution and EG are Pt/C:dry Nafion = 3:1 by weight, and EG:Nafion solution = 1:1 by volume.

The membrane was cut into  $6\text{ cm} \times 6\text{ cm}$  pieces, which were soaked in the solvent for at least 10 min to expand adequately the electrolyte membrane to the size of  $7.0\text{ cm} \times 7.4\text{ cm}$  (step 2 in Fig. 1). The membrane was then put in a holder, and residual EG on the surface was removed

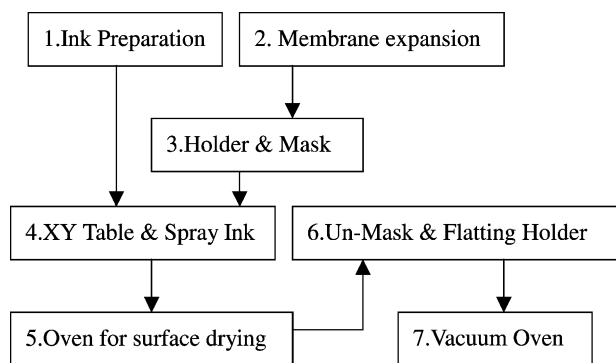


Fig. 1. Flow sheet for proposed MEA fabrication.

by wiping. Then, a mask with a  $5.6\text{ cm} \times 5.6\text{ cm}$  window was fixed to both sides of the membrane (step 3), and the catalyst ink was sprayed evenly on to both sides of the membrane under the control of an XY table (step 4). Thus, a catalyst layer with an effective area of  $5.6\text{ cm} \times 5.6\text{ cm}$  was formed on both sides of the membrane. The membrane was hung on a shelf which was placed in an oven for drying at a temperature below  $60^\circ C$  under atmospheric pressure (step 5). When the two surfaces had been evenly dried, the mask was removed (step 6) and the membrane was transferred to a vacuum oven at a controlled temperature below  $80^\circ C$  for at least 4 h (step 7). The catalyst layer finally shrank evenly to  $5\text{ cm} \times 5\text{ cm}$ .

The fabricated MEA was interposed between two uncatalyzed gas-diffusion electrodes (ELAT<sup>®</sup>, E-TEK) and assembled with conducting plates and graphite flow-field plates on two sides. Tightly with a torque wrench at 100 kgf cm, the unit was ready for testing. The flow-field plates used in the cell fixture were resin-impregnated graphite blocks (AXF-5QCF, POCO) with two-way-through serpentine patterns. Copper plates were employed as conductors and current-collectors. For comparison, a similar unit was assembled with electrode which contained  $0.40\text{ mg Pt cm}^{-2}$  (20 wt.% Pt/C on Vulcan XC-72, E-TEK). The electrodes were coated with Nafion solution by an automatic plotting system that could regulate the amount of coating by the applied solution. The temperature of the heating area was set around  $80^\circ C$  and a Nafion loading of  $0.67\text{ mg cm}^{-2}$  was applied in this work. The coated electrodes were then dried at  $70^\circ C$  for 1 h under vacuum. The MEA ( $25\text{ cm}^2$ ) was prepared by a hot-press method under 2000 lb force for 90 s at  $130^\circ C$ .

Table 1  
Test conditions for current–potential, ac impedance and cyclic voltammetric measurements

	(a) $H_2/O_2$	(b) $H_2/air$	(c) $H_2/air$	$H_2/air$ (ac impedance)	$H_2/N_2$ (CV)
Humidifier: $H_2/O_2$ (air) ( $^\circ C/^\circ C$ )	95/85	95/85	No	No	No
Backing pressure: $H_2/O_2$ (air) (psig/psig)	30/30	30/30	No	No	No
Cell temperature ( $^\circ C$ )	80	80	35	35	35
Flow rate: $H_2/O_2$ (air) (stoichiometric ratio)	1.5/2.0	1.5/2.0	1.5/2.0	4/14, 6 <sup>a</sup> /15 <sup>a</sup> (sccm $cm^{-2}$ )	6/6 (sccm $cm^{-2}$ )
Other conditions				0.9, 0.8 V; 1, 5 K <sup>a</sup> ; $\sim 0.5\text{ Hz}$	0.0~1.4 V; 20 mV $s^{-1}$

<sup>a</sup> This condition is used for E-TEK electrodes.

The test unit was connected to a test station (GT60, Globe Technology Inc.) for current–potential measurements. Both cyclic voltammetry and ac impedance methods were employed using a potentiostat (Autolab PGSTAT20 with BSTR10A, Eco Chemie B.V.) and an impedance analyzer (Autolab FRA2, Eco Chemie B.V.). The test conditions are given in Table 1. The electrochemically active surface (EAS) areas were obtained using a procedure previously reported [6,7]. The ohmic resistances were estimated directly from the Nyquist plots in the high-frequency region.

### 3. Results and discussion

The result of membrane expansion experiments are summarized in Table 2. It is clear that the relative increment of the full expansion volume is EG > glycerol > water, and the decrement of the shrinking volume is water > EG > glycerol. The order of the expansion:shrinkage ratio is glycerol > EG > water. Therefore, EG and glycerol are the two preferred candidates for solvent treatment, since they can also be used as dispersion agents in ink preparation. The glycerol shows the largest expansion:shrinkage ratio, but the soaking time is longer, which can be seen from the difference between the two volume increments in 10 and 45 min measurements. Because the boiling point of glycerol (290 °C) is higher than that of EG (198 °C), EG is easier to remove from the catalyst cast. Thus, it was finally decided to use EG in the experiments. In the expansion measurements, the *y*-direction (TD) is the most significant. In the drying process, however, the evenly cast catalyst confers equal shrinkage in both *x*- and *y*-directions. This makes the surface of the MEA uneven due to unequal shrinkage between the uncast portion of the membrane and the cast area. Nevertheless, the deviation is small for the 5 cm × 5 cm catalyst layer used in the fuel cell unit examined here. The measurements were also useful in deciding the painting size in the MEA process. Another interesting finding in the expansion experiments is that it is possible to improve shrinkage by treatment with two solvents. The membrane was first soaked in EG for 10 min, then transferred to water for 1 min. The shrinkage is less than about 2% compared with treatment in

only EG. The same result can be obtained by soaking the membrane in a mixture of 75% EG and 25% water. One possible explanation is that the water molecule on the membrane surface may block the vaporization of EG inside the membrane.

In ink preparation, the mixture was agitated by ultrasonic waves. A dispersing machine was also used to do the agitation. Although the latter might cause collapse of the Pt/C structure due to the mechanical shear stress, the cell performance of the electrodes by the two methods was found to be equal. The switch to a dispersing machine was undertaken in the interests of mass production.

The platinum loading of the cathode and anode in the prepared MEA are the same by using the same parameters in controlling the *XY* table and spraying nozzle. The loadings can be regulated from 0.05 to 0.4 mg Pt cm<sup>-2</sup> (20 wt.% Pt/C on Vulcan XC-72), which are deduced by weighing the difference between the dry membrane and the catalyzed membrane with given solid content for each spraying process. The more ink that is sprayed on the membrane, the longer the time required for the surface drying process. The drying temperature was set below 60 °C because the boiling point of methanol is 62 °C, and methanol is the major solvent of the Nafion solution. Vacuum drying at 80 °C can remove EG from the catalyst cast and membrane. This makes the cast shrink while restoring the membrane almost to its original dimensions. The shrinkage causes intimate contact not only at the interface of the catalyst and the membrane, but also between the catalyst particles in the cast since its structure has Pt/C surrounded with Nafion ionomer. The window size of the mask also depends on the spraying amount, but the influence on the final casting size is tolerable for small-sized MEAs.

Current–potential curves for the MEA fabricated by the proposed process are shown in Fig. 2 and are compared with those for E-TEK catalyzed electrodes. Under the operating conditions listed in Table 1, the performance of the MEA is generally better than the E-TEK electrodes. In fact, the loading of the electrode in the MEA is only 0.11 mg Pt cm<sup>-2</sup> (20 wt.% Pt/C on Vulcan XC-72), which is almost only one-quarter of the E-TEK. Thus, the present process effectively improves the performance of the fuel cell. To alleviate the

Table 2  
Membrane expansion/shrinkage measurements for 50 mm × 50 mm Nafion 117

Solvent	Time (min)	Measurements in solvents (mm)			Measurements in air (mm)			Volume increase <sup>a</sup> (%)	Volume decrease <sup>a</sup> (%)
		MD	TD	Z	MD	TD	Z		
Water	10	53.8	55	0.185	51.5	52	0.181	25.12	14.88
	45	54	55.5	0.190	50	50	0.175	30.16	23.17
EG	10	58	61	0.220	57.5	60.5	0.212	77.91	9.63
	45	58.5	62	0.225	56.5	59.5	0.210	86.53	13.49
Glycerol	10	53	53.5	0.200	56	57.5	0.205	29.62	0.49
	45	56	57.5	0.206	55.5	57	0.205	51.62	2.23

<sup>a</sup> Volume increase is based on 50 mm × 50 mm × 0.175 mm and volume decrease is based on measurement after 45 min in solvent.

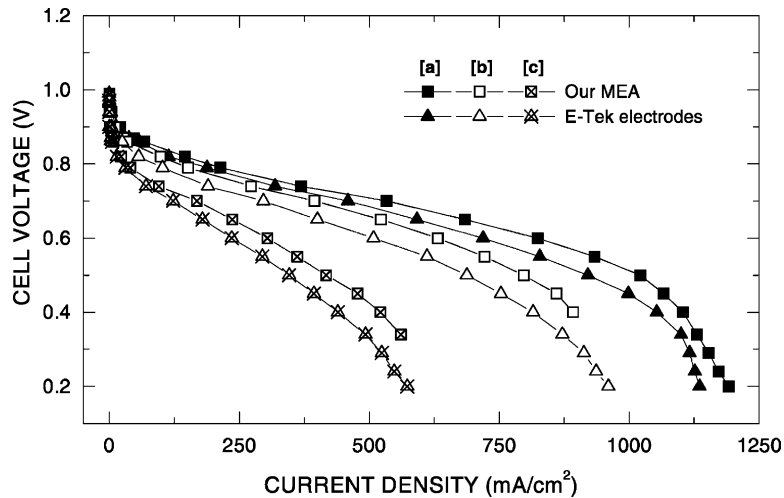


Fig. 2. Current–potential curves for conditions (a), (b) and (c) with two different electrodes.

influence of water shortage or flooding on the test cell, the current–potential curves in Fig. 2 were not obtained in the transient state by the scan method. Instead, the load bank was controlled at a certain constant voltage and the steady-state currents were averaged for each set point. When the voltage is set below the diffusion-controlled region ( $V < 0.5$  V), it is not easy to maintain the cell in a steady-state. Part of the curves is not shown in Fig. 2. Since the diffusion layers used in both test cells are the same, the trends in the diffusion-controlled region of current–voltage curves should be about equal. In the resistance-controlled region, the slopes of the present MEA are better than those of E-TEK catalyzed electrodes. This suggests that the shrinkage of MEA by the present process must have improved the contact between the particles and the ionomer, since the two test cells use the same membrane, viz. Nafion 117. The structure of the catalyst layer is fine and delicate, which effectively prevents the surface of the catalyst layer from chapping or being uneven. The layer enjoys close contact with the electrolyte membrane which increases the reaction activity. For a better understanding of catalyst utilization, kinetic parameters are quantitatively analyzed by the following equations:

$$E = E_o - b \log I - RI \quad (1)$$

$$E_o = E_r + b \log I_o \quad (2)$$

where  $E$ ,  $E_o$  and  $E_r$  are the cell potential, the open-circuit potential and the reversible potential, respectively;  $I_o$  the exchange current density for the oxygen reduction reaction;  $b$  the Tafel slope;  $R$  the cell resistance, which consists mainly of the ionic resistance of the electrolyte, the contact resistance between the cell components, and the mass-transport resistance in the electrode. These parameters were obtained by non-linear least squares fitting based on the Levenberg–Marquardt algorithm. Origin 5.0, Microcal software was used in the present study; the results are listed in Table 3. Under conditions (a)–(c), the values of  $E_o$  and  $R$  are found to decrease and increase, respectively.

This is reasonable since replacing  $O_2$  with air will induce greater resistance to mass-transport in the electrode. The parameters obtained under conditions (b) and (c) show less variation, which may be due to the uncertainty of the data acquisition, since the data measured fluctuate wildly when using air as the oxidant. With the present MEA  $E_o$ ,  $b$  and  $I_o$  exhibit good performance in the activation-controlled region (Table 3). Cyclic voltammetric data are presented in Fig. 3. Data for the electro-active surface area ( $m^2 g^{-1}$  Pt) are also used in Table 3. Cyclic voltammetric studies from 0.0 to 0.4 V provide information on the hydrogen adsorption and desorption which occurs on the platinum surface. The region from 0.4 to 0.5 V is regarded as the double-layer region [7].

Table 3  
Kinetic data of MEA

Electrode	Test condition	$I_{0.9\text{ V}}$ ( $mA\ cm^{-2}$ )	$I_{0.65\text{ V}}$ ( $mA\ cm^{-2}$ )	EAS area ( $m^2\ g^{-1}\ Pt$ )	Ohmic $R_{\Omega, 0.9\text{ V}}$ ( $\Omega\ cm^{-2}$ )	Tafel kinetic parameters			
						$E_o$ (V)	$b$ (V per decade)	$I_o$ ( $\mu A\ cm^{-2}$ )	$R$ ( $\Omega\ cm^2$ )
Present method	(a) $H_2/O_2$	20.8	684.2	84.11	0.49	0.979	0.058	40.1	0.23
	(b) $H_2/air$	11.1	522.3			0.975	0.067	136.2	0.25
	(c) $H_2/air$	1.6	236.5			0.916	0.065	12.8	0.44
E-TEK	(a) $H_2/O_2$	13.2	591.7	81.67	0.54	0.973	0.059	38.0	0.26
	(b) $H_2/air$	4.0	400.4			0.931	0.050	0.87	0.38
	(c) $H_2/air$	0.2	179.2			0.880	0.038	4.8E–6	0.87

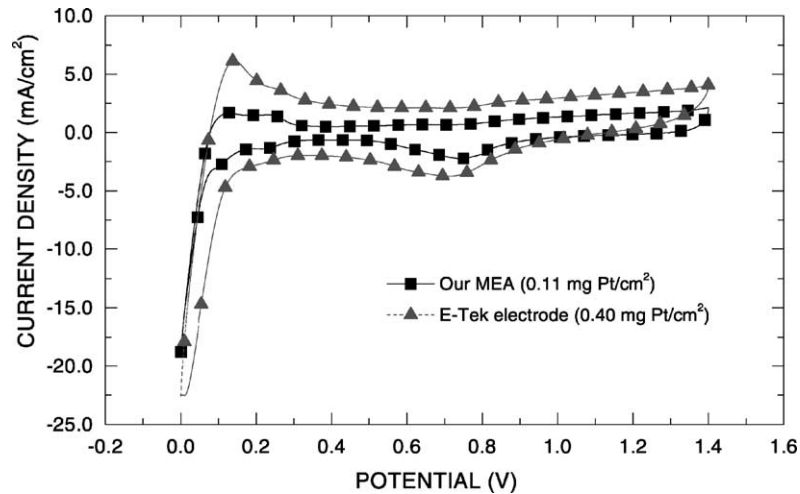


Fig. 3. Cyclic voltammograms for two different electrodes.

To evaluate the Pt surface area, the current densities of hydrogen adsorption and desorption were integrated separately and referred to a charge of  $210 \mu\text{C cm}^{-2}$ , which correlated to a mono-layer of hydrogen adsorption on the Pt surface [8]. Apparently, the present MEA has a smaller integrated area. The platinum loading is, however, much smaller than that of the E-TEK product ( $0.11 \text{ mg Pt cm}^{-2}$  versus  $0.40 \text{ mg Pt cm}^{-2}$ ), and thus the true reactive surface area is actually larger, namely,  $84.11 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$  versus  $81.67 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$ . Nyquist plots obtained by ac impedance for cells operated at 0.9 and 0.8 V are shown in Fig. 4. Since the two test cells use the same membrane and diffusion layers, low voltages (0.9 and 0.8 V) were selected to study the activation-controlled region. As expected, a semi-circular loop which corresponds to oxygen reduction is observed. An equivalent circuit  $R_{\Omega}(R_p C_{dl})$  can fit the characteristic of an electrochemical interface by non-linear regression, where  $R_{\Omega}$  represents the sum of electrode and electrolyte

resistance,  $R_p$  is the polarization resistance, and  $C_{dl}$  is the double-layer capacity [9]. The fitting result is given in Table 4. The ohmic resistance  $R_{\Omega}$  for each test cell is relatively constant and independent of the electrode overpotential. The MEA has a smaller  $R_{\Omega}$  than the E-TEK product. This trend is consistent with the current–potential data shown in Table 3. The polarization resistance is the sum of charge-transfer and diffusion resistance. Giorgi et al. [9] have claimed that a smaller semicircular loop indicates a faster charge-transfer reaction and a smaller  $R_p$  at low overpotential. In the present investigation, the  $R_p$  decrease rapidly as the electrode potential decreases from 0.9 to 0.8 V as shown in Table 4. Since the test flow rate for E-TEK is much higher than that for MEA, the comparison of  $R_p$  between these two test cells is not relevant. The double-layer capacity,  $C_{dl}$ , depends on the reactant concentrations and potentials. Although the flow rate of the E-TEK is higher, the MEA has a larger  $C_{dl}$  at 0.8 V. The results match

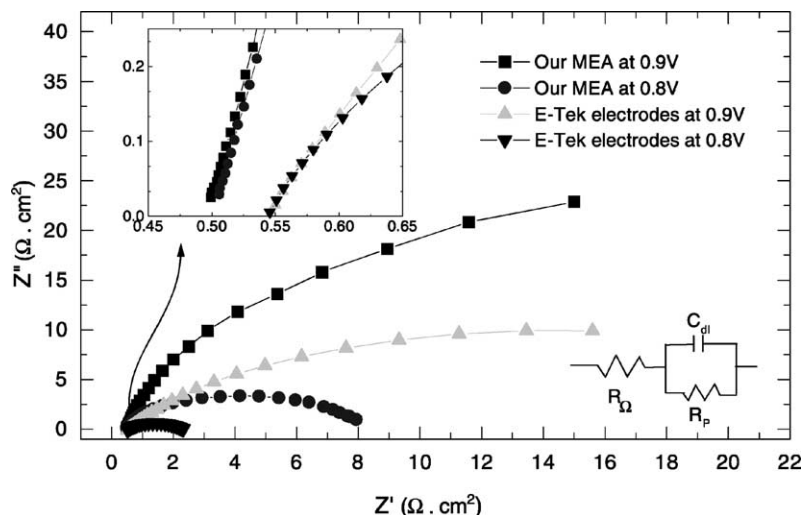


Fig. 4. The ac impedance Nyquist plots for electrodes operated at 0.9 and 0.8 V.

Table 4  
Parameter fitting of equivalent circuit  $R_{\Omega}$  ( $R_p C_{dl}$ )

	Present MEA		E-TEK electrode	
Electrode potential	0.9	0.8	0.9	0.8
$R_{\Omega}$ (m $\Omega$ )	19.6	20.0	21.6	21.6
$R_p$ (m $\Omega$ )	2460.0	279.5	627.0	60.7
$C_{dl}$ (mF)	158.1	147.2	177.3	140.3

well with electro-active surface area data obtained from cyclic voltammetric measurements.

#### 4. Conclusions

The coating process developed in this study overcomes the problem of membrane deformation and can be easily adapted for mass production. In addition, both sides of the membrane can be coated simultaneously and this makes the manufacturing process much simpler. The current density of the resulting MEA based on a  $H_2/O_2$  feed and operated at 0.65 V shows a 15.6% improvement over a commercially available MEA.

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