



Investigating the Timing Effect of the Nafion Addition to the Bimetallic (Pd-Pt) Catalyst in Proton-Exchange Membrane Fuel Cell Cathode

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ABSTRACT

In this research, bimetallic catalysts including Pd and Pt was synthesized on the composite of carbon nanotube (CNT) with Nafion and compared with Pd-Pt synthesized on CNT considering the key role of catalysts in PEMFC electrodes. The difference between the electrodes fabricated from these two synthesized catalysts was in the adding time of Nafion. The synthesized catalyst can enhance the performance of gas diffusion electrode (GDE) in cathode reaction (Oxygen Reduction Reaction or ORR) of polymer electrolyte membrane fuel cell (PEMFC) compared to commercial Pt/C catalyst. The bimetallic catalyst was synthesized in two steps. Pd and Pt were reduced at the first and second step, respectively. To reduce metals on support, the impregnation method were used along with hydrothermal. The electrochemical performance of the electrodes in ORR was studied through the Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS). Inductively coupled plasma (ICP), X-ray Diffraction (XRD), and Transmission Electron Microscopy (TEM) techniques were applied to characterize the catalyst. The results have confirmed that the timing of Nafion addition can influence the electrode performance for ORR.

1. INTRODUCTION

The fuel cell is widely considered as an energy converter system. The proton-exchange membrane fuel cell (PEMFC) has been developed due to several advantages such as the high efficiency, environmentally friendly, light weight, and low-temperature operation for portable applications [1-3]. The common catalyst used in the PEM fuel cells is platinum. One of the considerable barriers to economically use of PEMFCs is the cost of platinum. Currently, the major challenge in this field is to reduce the fuel cell energy cost by developing low-cost materials, processes, and components [4]. A practical way suggested in this regard is using the alloying Pt with other metals (Ni, Co, Pd, Ti, etc.) [5-7]. Both palladium and platinum belong to the same group in the periodic table. Therefore, they have very similar properties. The Pd activity for the ORR is slightly

lower than Pt. Moreover, the presence of Pd in ORR can improve the electrocatalytic activity of Pt [8-10]. The use of Pd with Pt may increase the corrosion resistance when they are used in an acidic medium of a proton-exchange membrane (PEM) fuel cell [11]. The catalyst utilization can be increased by using the catalyst supported on high surface area carbon and impregnation of a proton conductor into the catalyst layer of the electrode [12-14]. In this field, carbon nanotubes possess a remarkable property, including high electrical and thermal conductivities, mechanical strength, and large catalytic surface areas, which have potential uses in a proton-exchange membrane fuel cells (PEMFCs) [15]. Several types of research were investigated on the fact that that the Nafion loading in the catalyst layer effects the cell performance, distribution of pore size, and Pt surface area [16-18]. The presence of Nafion ionomer in the catalyst layer can increase the platinum utilization in the electrode,

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the catalytic activity of the three-phase zone, which help retaining moisture at high current densities and prevent membrane dehydration as well. To achieve the high catalyst performance, the Nafion loading in the electrode must be optimized. [19, 20].

In the previous study, it has been indicated that the timing of Nafion addition to the catalyst layer is very important and affects the performance of the electrode in ORR [18].

As mentioned above, a Pd-Pt catalyst was synthesized on the CNT-Nafion composite. The effect of Pd- Pt/CNT-Nafion composite on ORR was investigated. For this purpose, two bimetallic catalysts have been synthesized with different support (Pd-Pt/CNT and Pd-Pt/composite). Then, two electrodes have been fabricated using these synthesized catalysts. The performance of these electrodes in the ORR was compared with that with commercial catalyst 20%wt Pt/C. Furthermore, the electrodes were characterized with Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS), and catalysts characterization carried out by Inductively Coupled Plasma (ICP), Transmission Electron Microscopy (TEM), and X-Ray Diffraction (XRD). According to findings, the synthesized catalyst performance in ORR acted far better than Pt/C. For example, the current density at 0.3V of GDE1 is 58.66% higher than GDE2 and 117.7% higher than the commercial catalyst.

2. EXPERIMENTAL

2.1. Catalyst Synthesis

In this research, two catalysts were synthesized. One of the catalyst supports is the CNT (20-30nm Aldrich) and the other is the CNT-Nafion (%5 solution, Aldrich) composite.

In order to activate the surface, the CNTs were functionalized [21-23]. To this end, the CNTs were refluxed in 70% nitric acid (Merck) at 120 °C for 12h. Then, the solid phase was removed by centrifugation (ROTINA 46) and washed with distilled water. Finally, the recovered functionalized CNTs were dried at 80°C for 12h.

The composite was prepared from the functionalized-CNT and Nafion solution. The functionalized-CNT was mixed with Nafion solution in 2-propanol (Merck) and water (2:1 volume ratio). The mixture was sonicated (Misonix model S-3000) for 20 min. The prepared homogeneous suspension was dried at 70°C. According to the previous results, the optimal amount of Nafion in the composite was obtained [18]. Therefore, the same loading of Nafion was used in this research (1mg.cm⁻² in GDEs). At this step, the catalyst was deposited through the support. The dispersion of bimetallic catalyst was carried out step by step (two-step). In one

step, the appropriate amounts of palladium chloride (PdCl₂) precursor and an efficient amount of sodium citrate was dissolved in ethylene glycol (EG). This mixture stirred for 1h to entirely dissolve sodium citrate. Thereafter, the prepared composite was added to the mixture (for GDE1) and pretreatment CNT was added to the mixture (for GDE2). 5wt% KOH/EG solution was added drop by drop to raise pH adjustment to >10 under vigorous stirring. The mixture was then transferred into a Teflon-lined autoclave and conditioned at 130°C for 6h, followed by filtering, washing, and drying at 70°C. The Pd/composite and Pd/CNT were prepared.

At the second step, platinum chloride (H₂PtCl₆·6H₂O) precursor was treated by the same way as palladium was. However, Pd/composite or Pd/CNT was added here instead of CNT or composite.

Since the results of previous research [24] showed that the optimum atom ratio (Pd:Pt) was 3:1, this atom ratio was used in this research.

2.2. Gas Diffusion Electrode (GDE) Fabrication

In this study, the three-layer electrode was fabricated. The gas diffusion layer including carbon paper and microporous layer (TGPH-060T Toray) was used as a catalyst layer base.

A suspension was prepared by mixing the desired amounts of a synthesized Pd-Pt/composite (GDE1), glycerol (Merck), 2-propanol (Merck), and water to prepare the catalyst layer, and then, sonicated for 20min. This suspension was rolled into the diffusion layer; the electrode was dried at 70°C for 30min and then, at 120°C for 30min. The similar process was used to fabricate the GDE2. However, the synthesized Pd-Pt/CNT was used as the catalyst for GDE2 fabrication, and Nafion solution (5% from Aldrich) was added to prepare a suspension. In fact, Nafion was added in GDE1 before the Pd and Pt reduction (Nafion presence in catalyst support), but in GDE2, Nafion is added when the catalyst suspension is being prepared. The GDE3 was fabricated similar to GDE2 instead of synthesized catalyst the commercial Pt/C was used though.

2.3. Physical Properties

The amount of reduced Pd and Pt on each applied catalyst support were determined using the inductively coupled plasma (ICP) technique (ICP-AES, 314, Switz). To implement these measurements, 5mg of each synthesized catalyst was dissolved in a separate container in a mixture of HCl and HNO₃ (3/1). These solutions were used in ICP measurements.

The x-ray powder diffraction (XRD) pattern of the Pd-Pt/CNT was recorded by Philips PW 3710 using filtered Cu K α radiation at 40kV and 40mA. 2 θ angles were scanned from 20° to 90°. The morphologies of the

catalysts were analyzed via the transmission electron microscope (CM Philips 30).

TEM images were prepared via the transmission electron microscope (CM Philips 30).

2.4. Electrochemical Measurement

An EG&G Princeton Applied Research Model 2273 instrument was used to investigate the electrochemical properties of the GDEs. The electrochemical analysis of GDEs (geometric exposed area 1cm^2) was carried out at 25°C and $2\text{M H}_2\text{SO}_4$ solution. All measurements were performed in a conventional three-electrode cell with O_2 flowing for linear sweep voltammetry (LSV), impedance spectroscopy, Ar flowing for cyclic voltammetry (CV), and ionic resistance measurement. An Ag/AgCl was used as the reference electrode and a platinum flat electrode was employed as the counter electrode.

The AC Electrochemical Impedance Spectroscopy (EIS) method was used to perform a GDEs resistance for ORR. In the Nyquist plot of the semicircle diameter, R_p is the polarization resistance. The sum of the electrolyte and electrode resistance Nyquist plot was subtracted for these GDEs. The impedance measurement was studied at 0.4 V vs Ag/AgCl potential to obtain R_p . This potential was in ohmic resistance region. The frequency range was 10kHz to 100mHz interval and AC potential amplitude was 5mV . The impedance measurements were used to characterize the ionic resistances of GDEs. A Warburg-like response (45° slope), which illustrated the occurrence of ion migration through the catalyst layer, can be observed at low frequencies. The length of the Warburg-like region projected onto the real impedance (Z_{real}) axis is proportional to the ionic resistance R_{ion} [25-27]. The impedance measurement was studied in OCV potential (10kHz - 0.1Hz) and Ar atmosphere to obtain R_{ion} .

3. RESULTS AND DISCUSSION

There are three participants in the PEMFC process in electrochemical reactions including gases, electrons (from solid phase), and protons (liquid phase). The reaction takes place when all species are available on the catalyst surface. The electrons travel through the catalyst solids, so the catalyst particles need to be electrically connected to the substrate. Protons travel

through the Nafion ionomer, so the catalyst must contact with the Nafion. Finally, the reactant (gas phase) travel through voids, so the GDE must be sufficiently porous to allow gases to travel to the reaction sites (catalyst). Hence, the reactions take place at a three-phase zone between Nafion (liquid), catalyst (solid), and void (gas) [28].

The ICP results illustrated that the synthesized samples contained 18wt% catalysts (instead of the 20wt% based on precursor). The percentage of synthesized catalysts is listed in Table 1.

The typical XRD pattern of Pd-Pt/CNT catalyst is shown in Figure 1. The peak centered can be ascribed to the (002) planes of CNT support at about 25° . The ones at 40 , 47 , 68 , and 85 are associated with the (111), (220), (200), and (311) planes of FCC (Face-Centered Cubic) Pt, respectively.

The peak is broadened when the catalyst particles are in nanometer-scale because Pt and Pd have the same crystal structure (FCC), which are very close lattice parameters, and their sets of diffraction peaks are overlapped. Since the Pt particles were reduced after Pd reduction, the XRD pattern can be attributed to the Pt, and the presence of Pd can affect the d-spacing and slightly shifting the peaks of Pt [24]. Considering the electrochemical results of GDEs, catalyst support changes will affect the electrochemical behavior of active species at the GDE surface.

Cyclic voltammetry was employed to measure the electroactive surface area (EAS) (Figure 2).

TABLE 1. Name of electrode and molar ratio of the synthesized catalyst

GDE name		1	2	3
Catalyst support		Composite (Nafion/CNT)	CNT	Vulcan
Pd:Pt		3:1	3:1	Commercial catalyst
precursor	%Pd	75	75	0
	%Pt	25	25	100
ICP	%Pd	73.6	72.8	-
	%Pt	26.4	27.2	-

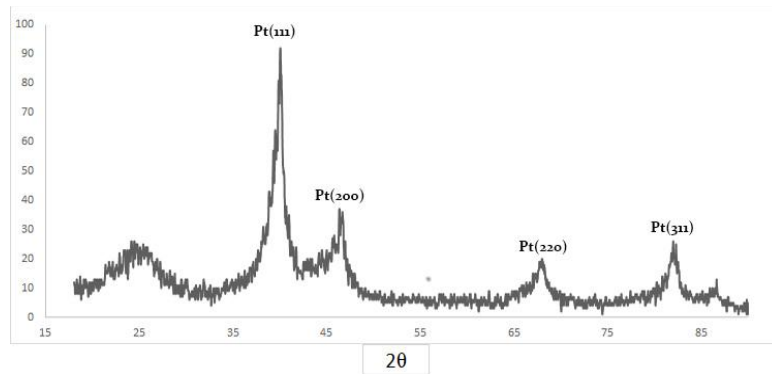


Figure 1. The XRD pattern of Pd-Pt/CNT

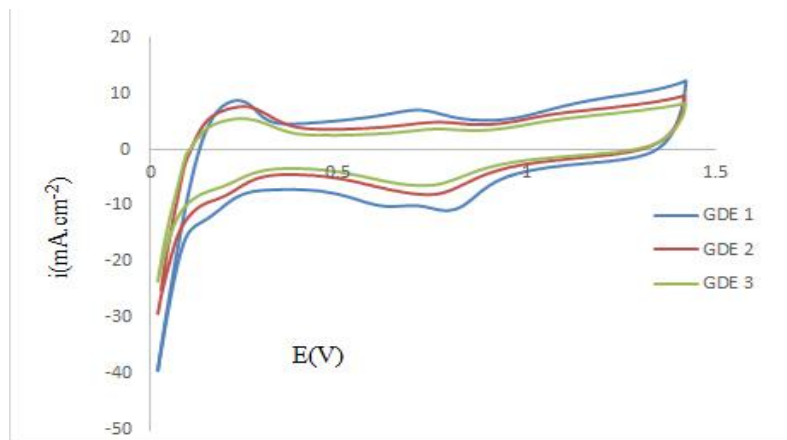


Figure 2. Cyclic voltammetry of GDEs in 2 M H₂SO₄, argon atmosphere, 50 mV.s⁻¹ scan rate and 25°C

Moreover, the coulombic charge of hydrogen desorption of each GDE was used to calculate the EAS (Table 2) [29]:

$$EAS = \frac{Q_h}{0.21 \times [\text{catalyst}]} \quad (1)$$

Where Q_h is the charge for hydrogen desorption (mC.cm⁻²), [catalyst] is the catalyst loading (mg.cm⁻²), and 0.21 (mC.cm⁻²) is the charge required to oxidize a monolayer of H₂ on bright catalyst. The roughness factor (R_f) can be calculated by the following equation:

$$R_f = \frac{EAS}{s} \quad (2)$$

Where S is the geometric surface area (m².g⁻¹). These catalysts demonstrate the adsorption-desorption peak, which confirms that the catalyst is active. The active surface area of catalysts is tabulated in Table 2. The access of high EAS could be attributed to the good formation of the three-phase zone.

TABLE 2. Exchange current density, Tafel slope, transfer coefficient α_c , the current density at 0.3 V, charge transfer resistance, and ionic resistances of all fabricated GDEs

GDE	$i_0 \times 10^{-5}$ (A.cm ²)	b (mV.de ⁻¹)	α_c	i at 0.3(V) (mA. mg _{cat} ⁻¹)	EAS (m ² .g ⁻¹)	R_f	R_p (ohm)	1/3 (ohm)	R_{ion}
1	31.18	41.27	1.43	806.28	184.39	1.48	0.89	1.41	
2	17.39	52.45	1.18	508.16	137.52	1.26	1.35	1.73	
3	9.51	50.19	1.03	370.36	106.95	1.12	1.79	3.92	

According to the EAS results, increasing the performance of the electrode for ORR is due to the development of the three-phase zone. These results indicate that the performance of GDE1 is better than GDE2. This preference of GDE1 is ascribed to better catalyst accessibility; in other words, when the Nafion-CNT composite is used as the catalyst support (in GDE1), the accessible catalyst surface is greater than the GDE2. In GDE2, the surface of catalyst particles may be blocked by the Nafion ionomer. Therefore, the Nafion used in catalyst support (GDE1) can be improved the accessibility of catalyst particles for the reactant, and accordingly, the EAS is enhanced.

The polarization and ionic resistance of GDEs were obtained by using the electrochemical impedance spectroscopy in a different condition. All results are reported in table 2. The AC impedance spectrum of each GDE was obtained to achieve more information about the GDEs. The data resulted from the analysis were plotted in the Nyquist representation, although the Nyquist plots were semi-circular. This shape of Nyquist plots points out to the equivalent circuit represented in Figure 3. The diameters of the semi-circles for each GDEs are significantly different. As shown in Figure 3 and Figure 4, the charge transfer and the ionic resistance of GDE1 had a minimum value, respectively.

The lower resistance of the GDE1 and the GDE2 compared to the GDE3 can be attributed to the difference in catalyst base and the effect of the presence of palladium on the catalyst layer. Among these three GDEs, the GDE1 shows the lowest resistance. Such this capacity can be the result of the timing of Nafion addition to the catalyst layer. In other words, the ionomer may block the catalyst sites in the case of GDE2, so the resistance of electrode GDE2 is higher than GDE1.

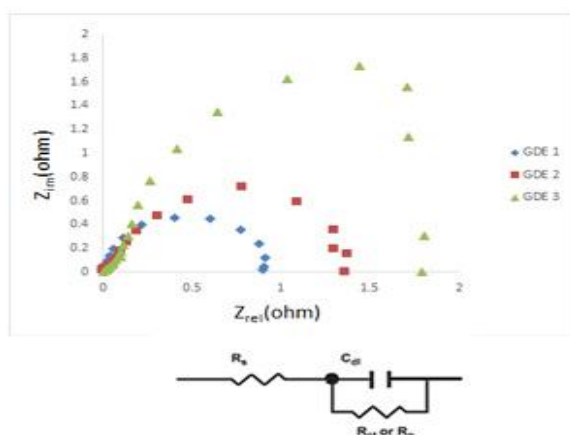


Figure 3. Nyquist plots of the impedance responses from 10kHz to 100mHz for GDE1 ◆, GDE2 ■, GDE3 ▲ in 2M H₂SO₄ at 400mV, 25°C, and equivalent circuit

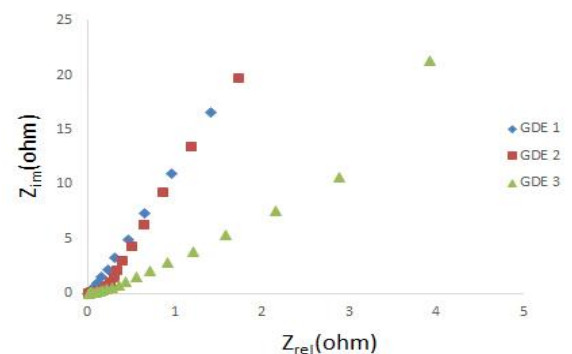


Figure 4. Nyquist plots of the impedance responses from 10kHz to 100mHz for GDE1 ◆, GDE2 ■, GDE3 ▲ in 2M H₂SO₄ at OCV, Ar atmosphere, and 25°C

The kinetic parameters of the ORR for a GDE can be obtained from the I-V curve (Figure 5).

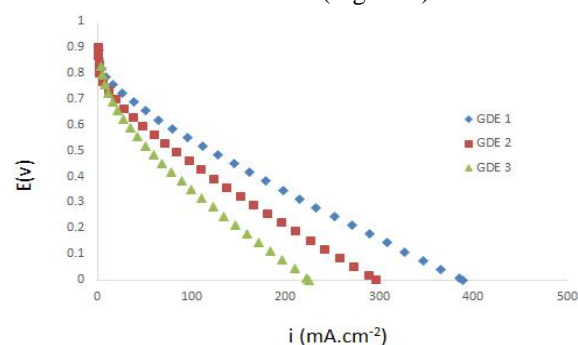


Figure 5. LSV curve GDE1 ◆, GDE2 ■, GDE3 ▲ in 2M H₂SO₄, 5mV.s⁻¹ scan rate, and 25°C

The investigation of the experimental polarization data was performed using the Tafel equation [29]:

$$\eta = E - E_{eq} = -\frac{2.303RT}{nF\alpha_c} = -b \log \frac{i}{i_0} \quad (3)$$

where η is the over-potential, E_{eq} is the open-circuit voltage, R is a gas constant, T is a temperature, n is a number of electrons, F is a faraday constant, α_c is a cathodic transfer coefficient, b is the Tafel slope, i is the current density, and i_0 is the exchange current density for the ORR. The kinetic parameters of the ORR for the GDEs can be obtained from the I-V curves and Equation 3.

The exchange current density indicated that the reaction rate on the electrode surface is an important kinetic parameter. The Tafel slope (b) at high current density is proportional to activation loss in the polarization curve. Therefore, the small b indicates lower activation loss, which determines a better performance for the electrode (Table 2). These results (Table 2) indicate that GDE1 shows the best

performance than the others. An environment needs to be created with a triple interface contained Nafion, catalyst, and oxygen to obtain the maximum efficiency. Therefore, it has been concluded that the triple-zone is more available in GDE1 with the optimum amount of Nafion. As mentioned previously, the ORR rate and also the current density is improved because the catalyst accessibility in GDE1 is better than GDE2.

All electrochemical results can be proved by TEM images of GDE1 catalyst layer in Figure 6.

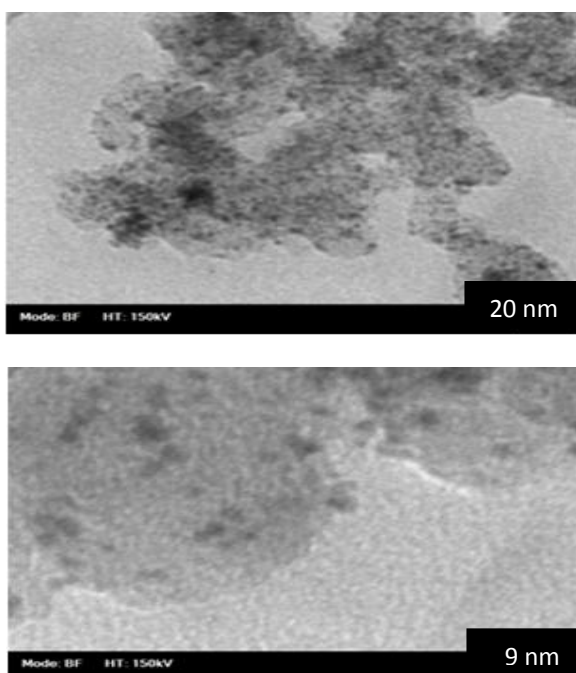


Figure 6. TEM image of Pd-Pt/composite catalyst with different magnification

The TEM images of GDE1 demonstrated that the particle size of the catalyst is on the nanometer scale. The proper dispersion of nanoparticle can cause the expansion of the three-phase zone, which improves the performance of GDE1 in ORR.

4. CONCLUSION

As regards, three phases of species, namely gases, electrons (solid), and protons (liquid) participated in the electrochemical reaction. The reaction can take place on the catalyst surface where they have access to all three species. The synthesized bimetallic catalysts were prepared using the impregnation and hydrothermal method with different support. Then, the synthesized bimetallic catalyst and commercial Pt/C

catalyst were compared. It has been indicated that the timing of Nafion addition to the catalyst layer is very important and prepared electrode (GDE1) exhibited excellent performance in the ORR. One of the enhanced parameters is EAS. The EAS in GDE1 was 34.1% better than GDE2 and 72.4% better than the commercial catalyst. The ICP results indicated that the Pd and Pt particles were reduced successfully onto the Nafion-CNT composites as well as the CNTs.

Therefore, the applied method is appropriate to synthesis catalyst. The TEM images represented that the catalyst was dispersed on support very well, and the catalyst particle sizes were nanometer. The electrochemical results, such as the current density at 0.3V illustrated that the reduction of Pd-Pt on Nafion-CNT composite (namely the GDE1) exhibited better performance in the ORR than Pd-Pt on CNTs (GDE2) and the commercial catalyst (GDE3), which illustrated that this current density of GDE1 is 58.66% higher than GDE2 and 117.7% higher than commercial catalyst. Among these three GDEs, the charge transfer resistance of GDE1 is lower. The superior performance of this electrode can be attributed to better reactant accessibility to the three-phase zone. Accordingly, the reported synthesis technique can be used as a good method for the preparation of carbon-supported metal particles from metal precursors.

5. Appendix. Nomenclature

A	Geometric area of electrode
b	Tafel slope
CNT	Carbon nanotube
EAS	Electroactive surface area
E_{eq}	Equilibrium potential
E	Electrode potential
F	Faraday constant
GDE	Gas diffusion electrode
i	Current density
i_0	Exchange current density
MEA	Membrane electrode assembly
MPL	Micropore layer
n	Number of electrons
OCV	Open circuit voltage
R_p	Polarization resistance
R_f	Roughness factor
S	Catalyst surface area
α_c	Cathodic transfer coefficient
η	Over-potential

6. ACKNOWLEDGEMENTS

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