

## Supporting Information

### **Co-assembled conducting polymer for enhanced ethanol electro-oxidation on Pt-based catalysts**

**Le Quynh Hoa,<sup>a</sup> Hiroyuki Yoshikawa,<sup>a</sup> Masato Saito<sup>a</sup> and Eiichi Tamiya<sup>\*a</sup>**

<sup>a</sup> *Department of Applied Physics, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.*

*Fax: 81 6 6879 7840; Tel: 81 6 6879 4087;*

*E-mail: tamiya@ap.eng.osaka-u.ac.jp*

## 1. Experimental

Reagent grade aniline, concentrated nitric acid, glycerol, camphorsulfonic acid (CSA), ammonium peroxydisulfate (APS) and Multi-walled carbon nanotubes (MWNTs, purity  $\geq 95\%$ , 40-70 nm in diameter) were obtained from Wako Co., Japan. The electrocatalyst precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) and poly(pyrrole) in doped state (5% in water) were purchased from Aldrich, USA. MWNTs were surface oxidized by refluxing in conc.  $\text{HNO}_3$  solution at  $140^\circ\text{C}$ - $160^\circ\text{C}$  for 24 h, and then decorated with Pt-NPs by refluxing with  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in aqueous glycerol at  $140^\circ\text{C}$ , pH 10 for 12 hours followed by filtering and vacuum drying. The loading of Pt was adjusted to  $\sim 20\%$  mass of Pt/MWNTs.

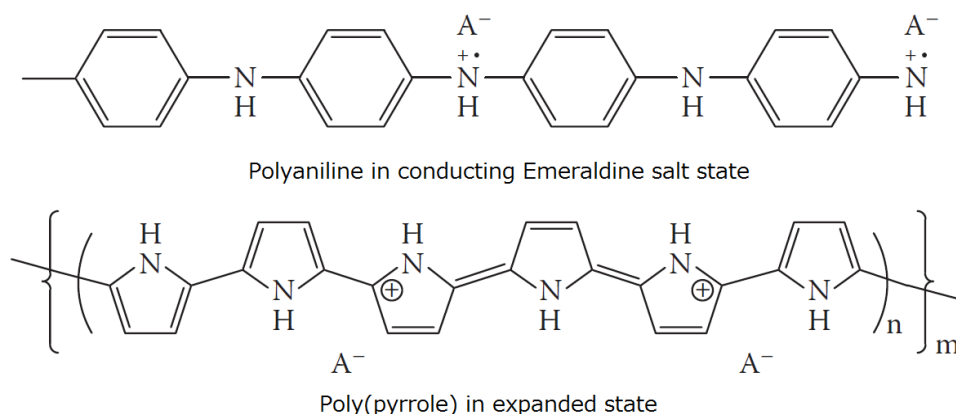
The chemical polymerization of PANI was carried out at room temperature using a rapid mixing method. In brief, aniline was diluted with aqueous 1 M CSA. A separate solution of APS with the concentration four times reduced of aniline, was prepared in the similar aqueous 1 M CSA. The two solutions were then combined and mixed with a magnetic stir-bar for one minute and then allowed to react undisturbed overnight. The resulting green emeraldine salt PANI was then purified via a series of centrifugations, and dried up for further uses.

Fabrication of the catalyst on C paper substrates was done by dispersing 5 mg Pt/MWNTs into 1 mL ethanol and 50  $\mu\text{l}$  nafion (5%, Wako Co., Japan), which was then casted onto the surface of carbon paper to obtain a total Pt loading of  $50 \mu\text{g cm}^{-2}$ . The electrodes were dried and used for conducting polymer deposition by directly casting. The concentration of dispersed PANI and PPY was  $5 \text{ mg mL}^{-1}$  of ethanol 99.5% and deionized water, respectively. The co-assembled PANI-PPY suspension was simply made by mixing these two native polymer solutions with varying volume ratios to get different weight ratios between PANI and PPY. The electrodes were then subjected to thermal treatment at  $80^\circ\text{C}$  for an hour.

The surface morphologies of various conducting polymer-supported Pt-MWNTs on C paper were acquired by scanning electron microscopy (SEM) (DB 235 microscope, FEI). Electrochemical measurements were performed with an Autolab potentiostat/galvanostat PGSTAT12 (EcoChemie, Netherlands). A standard three-electrode cell was used for the electrochemical measurement of catalysts at room temperature. A platinum spiral wire served as a counter electrode and all potentials were measured with respect to Ag/AgCl reference electrode. Impedances were measured under quiet

condition using four bias potentials within the ac frequency range of 100,000 to 0.1 Hz with an excitation signal of 10 mV.

## 2. Structures of PANI and PPY in doped states

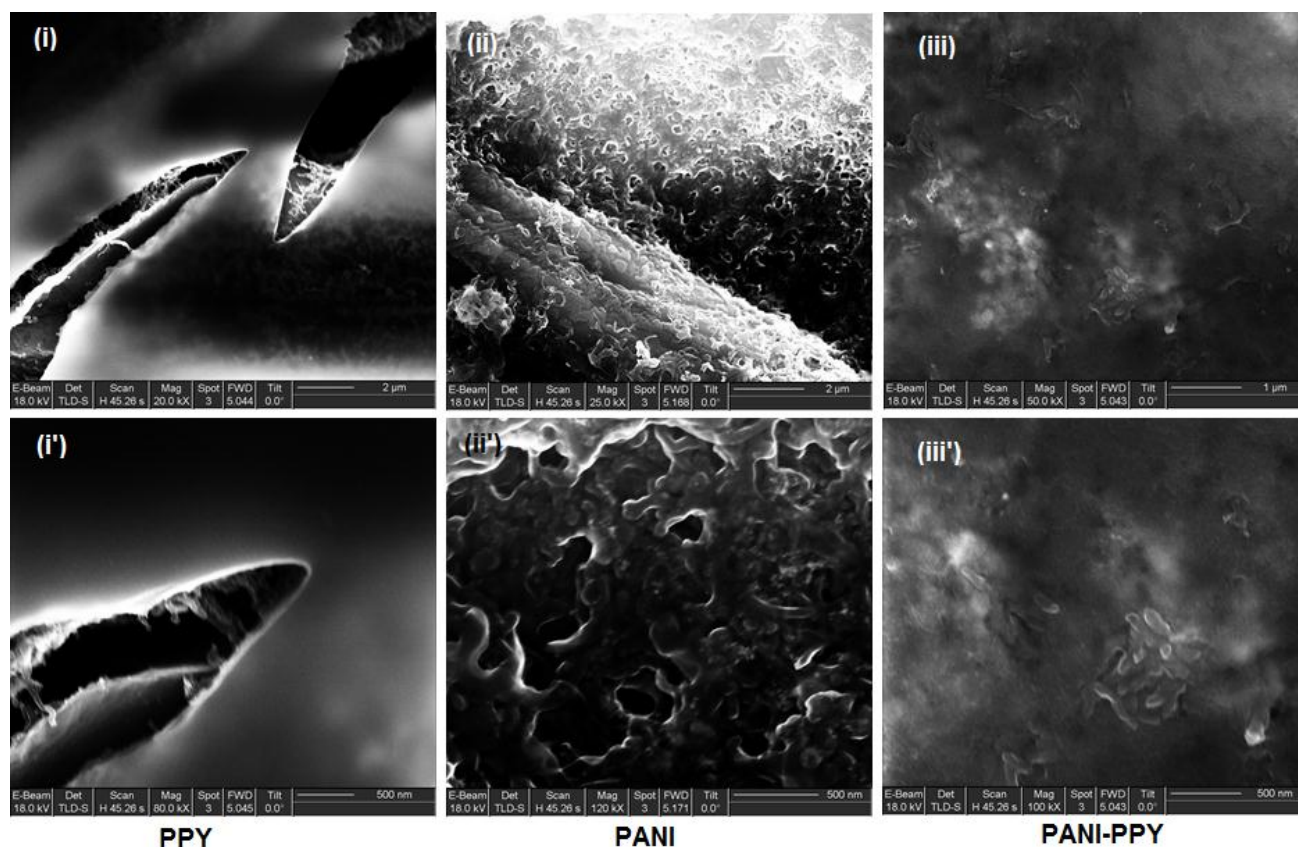


**Fig. S1.** Structures of polyaniline and poly(pyrrole) in doped states.

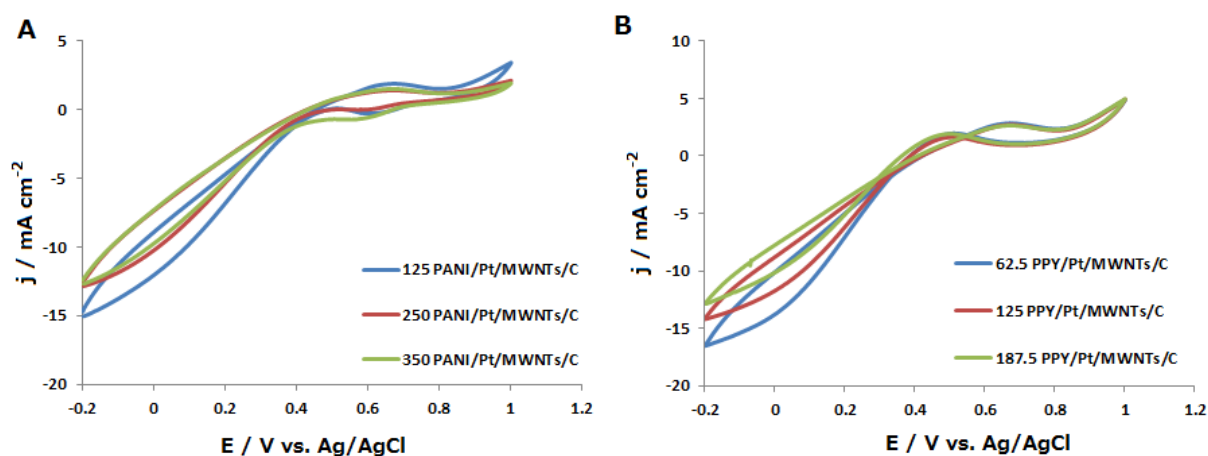
Herein, the PANI and PPY structures were simplified by hiding the cross-linked and branched structures formed during polymerization and thermal treatment.  $\text{A}^-$  is the dopant counterion or anions in electrolyte such as  $\text{ClO}_4^-$ , and might be  $-\text{OH}$  of water via hydrogen bonding (in case of PANI only). In the main manuscript the “native form” of PANI and PPY is used to denote the polymer itself as sole component casted on the Pt/MWNTs/C to form either PANI/Pt/MWNTs/C or PPY/Pt/MWNTs/C, and the “assembly form” PANI-PPY is used to denote the mixture of PANI and PPY casted on Pt/MWNTs/C to form co-assembled PANI-PPY/Pt/MWNTs/C.

## 3. Optimization of polymer loading on electrode surface

To obtain the optimized polymer loading on the surface of electrode, we examined the concentration of PANI and PPY in native forms from  $2.5 \text{ mg mL}^{-1}$  to  $10 \text{ mg mL}^{-1}$ , resulted in the loading of polymer from  $0.125 \text{ mg cm}^{-2}$  up to  $1 \text{ mg cm}^{-2}$ . After fabrication, the polymer coated electrodes were subjected to cyclic voltammetry to investigate their electrochemical responses toward ethanol oxidation reactions. The samples also have been examined the structural morphology by scanning electron microscopy (SEM) (DB 235 microscope, FEI). We presented here the structural morphology of the high loading samples for both native and co-assembled polymers coated Pt/MWNTs/C.



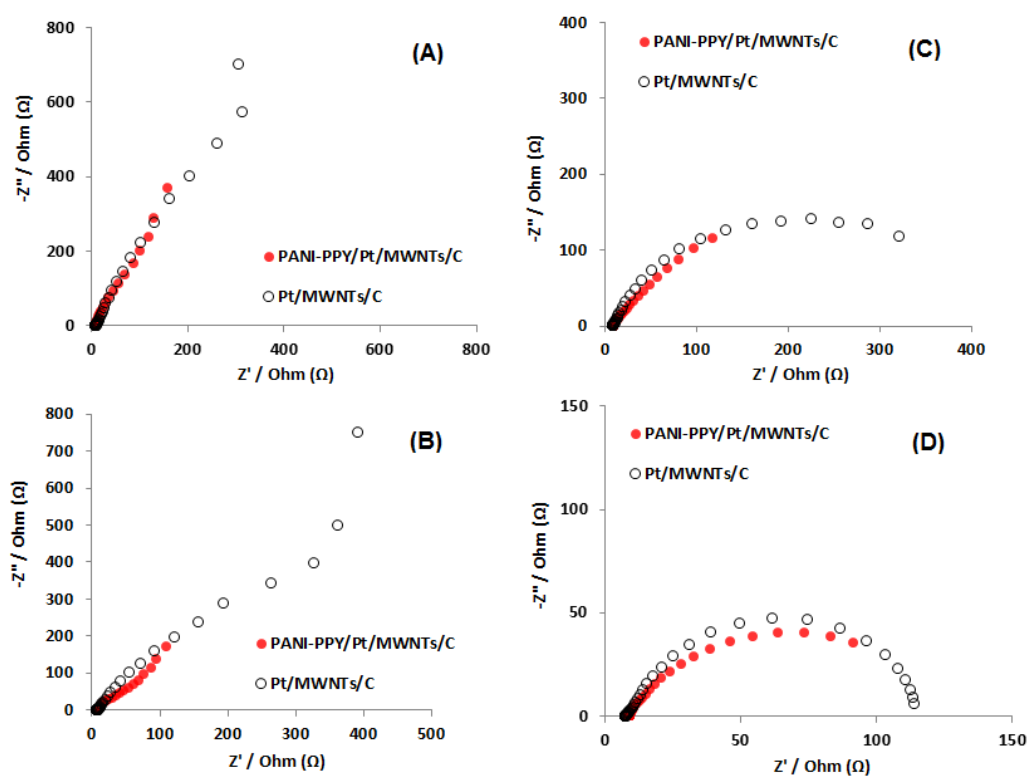
**Fig. S2.** Structural morphology of high loading PPY (i and i'), PPY (ii and ii'), PANI-PPY (iii and iii') coated Pt/MWNTs/C. The polymer loading in all cases is  $350 \mu\text{g cm}^{-2}$ . The weight ratio of PANI to PPY is 1:1.



**Fig. S3.** The fifth cyclic voltammograms of various loading of PANI ( $125$  to  $350 \mu\text{g cm}^{-2}$ ) and PPY ( $62.5$  to  $187.5 \mu\text{g cm}^{-2}$ ) coated Pt/MWNTs in  $0.5 \text{ M C}_2\text{H}_5\text{OH}$  in  $0.1 \text{ M HClO}_4$ . Scan rate is  $50 \text{ mV s}^{-1}$ . Loading of Pt is  $0.05 \text{ mg cm}^{-2}$ .

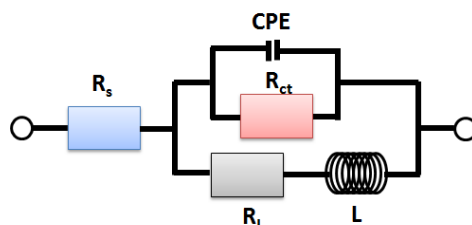
In native form, less than  $125 \mu\text{g PANI cm}^{-2}$  and  $62.5 \mu\text{g PPY cm}^{-2}$  loading resulted in partly covered Pt/MWNTs/C and therefore unstable CVs data, thus it is not presented here. Increasing the polymer loading caused the significantly thick layer covered the Pt/MWNTs (Fig. S2), thus inhibited the Pt active site, resulting to the lower current density of ethanol oxidation peaks (in case of PANI) or increase the ratio  $I_f/I_b$  (in case of PPY) in relevant CVs (Fig. S3). Consequently,  $125 \mu\text{g cm}^{-2}$  is the optimized loading of PANI and PPY. Increasing the cycle number also resulted in the increase of the difference between the various loading samples since the intermediates adsorption increase with reaction time, thus instead of 5<sup>th</sup> cycles, the 30<sup>th</sup> cycles were used to further analyze the electrochemical responses of the optimized samples (Fig. 2).

#### 4. Electrochemical Impedance Spectroscopy



**Fig. S4.** Electrochemical impedance spectra at different applied potentials on Pt/MWNTs/C and PANI-PPY/Pt/MWNTs/C catalysts in 1 M  $\text{C}_2\text{H}_5\text{OH}$  and 0.1 M  $\text{HClO}_4$ . (A) 0.7 V, (B) 0.6 V, (C) 0.5 V and (D) 0.4 V. The data was taken after applying 10 cycles CVs in 0.1 M  $\text{HClO}_4$ .

Electrode properties were characterized using Nyquist plots from EIS measurements (Fig. S4) to better elucidates the interaction between electrolyte, electrode surface, and charge transfer inside catalyst structure. The total impedance of this system can be described by the equivalent circuit in Fig. S5.

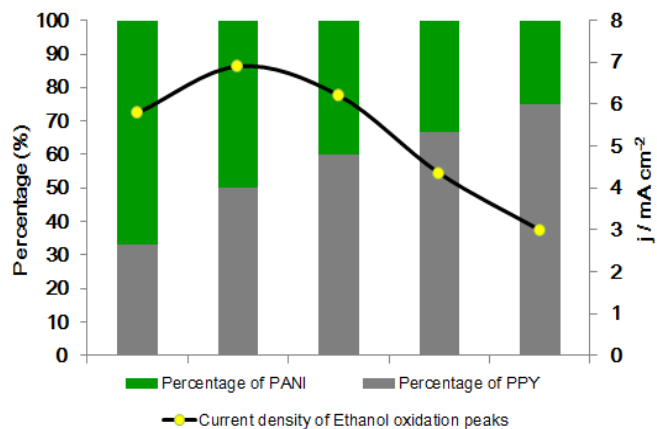


**Fig. S5.** Equivalent circuit used for the fitting of impedance spectra in Fig. S3.  $R_s$  is the solution resistance, CPE is the constant phase element representing the double-layer capacitance,  $R_{ct}$  is the charge transfer resistance,  $R_L$  is the resistance of adsorbed layer and L is the inductance of the adsorbed layer.

From Fig. S4, an alteration in the impedance spectrum of both Pt/MWNTs/C and PPY-PANI/Pt/MWNTs/C electrodes is evident following the change of bias potentials applied for the measurement. The total resistance increases (larger semicircles) with the increase in potential within 0.4V and 0.7V vs. Ag/AgCl due to increasing of  $R_{ct}$  and  $R_L$ . This reveals a slow reaction rate of ethanol oxidation caused by the poisoning of reaction intermediates, which is strongly adsorbed on Pt and blocks incessant adsorption and dehydrogenation of ethanol. Thus, the increase of resistance could be attributed to increasing coverage of intermediates.

Specifically, from 0.4 V to 0.5 V, PANI-PPY/Pt/MWNTs/C demonstrates the smaller semicircle resulted from smaller charge-transfer resistance than that of Pt/MWNTs, indicating the faster kinetic of ethanol oxidation on the surface of electrode. From 0.6 V to 0.7 V, in case of Pt/MWNTs/C, the Nyquist plots start flipping toward the second quadrant of the complex plane, indicating the passivation of electrode surface, while PANI-PPY/Pt/MWNTs/C remained observable higher knee frequencies. It means that co-assembled conducting polymer does not only enhance the charge-transfer and therefore reaction kinetics, but also contribute to the depoisoning of the catalyst surface.

**5. Effect of weight ratio between PANI and PPY in the co-assembled form on maximum current density of ethanol oxidation.**



**Fig. S6.** Effect of weight ratio between PANI and PPY in the co-assembled form (deposited on Pt/MWNTs/C) on maximum current density of ethanol oxidation. Electrolyte is 0.5 M  $\text{C}_2\text{H}_5\text{OH}$  in 0.1 M  $\text{HClO}_4$  and scan rate is  $50 \text{ mV s}^{-1}$ . Loading of Pt is  $0.05 \text{ mg cm}^{-2}$ . The data was taken from the fifth cycles of each sample's voltammetry.