Supporting Information

The Exceptional Tandem Catalyst Pt_1Pd_1 NPs Embedded on Fe_3O_4-Polypyrrole Composite Serving for Both Ethanol Oxidation Reaction and Oxygen Reduction Reaction in Direct Ethanol Fuel Cell

Rajib Adhikary[1, 2] and Jayati Datta*[1]

[1] Department of Chemistry, Renewable Energy Research Centre, Heritage Institute of Technology, Kolkata-700107, West Bengal, India

[2] Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711103, West Bengal, India

* Corresponding author e-mail: jayati.datta@heritageit.edu; jayati_datta@rediffmail.com

Experimental Section

Synthesis of Carbon/ PPy-Fe_3O_4 supported catalyst matrices

A known quantity of Pyrrole (Alfa Aesar, 98+ % pure) was syringed into an aqueous suspension containing a definite amount of Fe_3O_4 powder (Sigma–Aldrich, USA, 98+% pure). The system was cooled in an ice-bath for 30 min. A known amount of Potassium perdisulfate (Merck, Germany) was added to initiate oxidative polymerization of Pyrrole under vigorous mechanical shaking. The solution turned green immediately and then black, indicating the formation of Poly-pyrrole (PPy). After 1 h the total black mass was collected by filtering and washing the reaction mixture with deionized water and methanol (Loba Chemie) and dried under vacuum at 90^{o}C for 6 h. The composite matrix PPy-Fe_3O_4 thus formed was used as support to decorate Pt and PtPd NPs separately using $NaBH_4$ (Merck, Germany) reduction scheme with the respective precursors H_2PtCl_6 and $PdCl_2$ (Arora Matthey Ltd.) taken in proportionate concentrations. The binary catalysts on carbon support (PtPd/C) were also prepared for comparing the electrochemical output parameters of the PPy-Fe_3O_4 supported catalysts in this investigation.

The single Pt and binary PtPd catalysts on Vulcan XC-72 carbon and PPy-Fe_3O_4 support (Pt/C, PdPt/C, Pt/ PPy-Fe_3O_4 and PtPd/ PPy-Fe_3O_4) were synthesized under $NaBH_4$ reduction scheme by using respective precursor salts maintaining Pt: Pd molar ratios of 1:1 in the chemical bath. Initially requisite amount of support materials were dispersed in ethanol-water mixture by stirring and sonication. Subsequently Pt and Pd precursors, $H_2PtCl_6.6H_2O$ and Pd precursor, $PdCl_2.2H_2O$ (Arora Matthey Ltd., India) in appropriate concentrations (less than 0.005 mol L^{-1}) were added to the support suspension under constant stirring and sonication, alternately for 3 hours. Thereafter required amount of $NaBH_4$ (Merck, Germany) solution were added drop by drop, to the mixture with vigorous stirring for the complete reduction of metal precursor salts. The resulting mixture was centrifuged and washed with de-ionised water several times to make it chlorine free. The residue was then dried in oven for 4 hours at 80 ^oC to obtain the Pt and PtPd catalysts supported on carbon and PPy-Fe_3O_4. The respective catalysts-support materials were designated as Pt/C, PtPd/C, Pt/ PPy-Fe_3O_4 and PtPd/ PPy-Fe_3O_4.

Materials Characterization

X-ray diffractograms (XRD) of the electro-catalysts were obtained through SEIFERT-2000 diffractometer operating with CuK_α radiation (λ = 0.1540 nm) generated at 35 kV and 30 mA. Scans were done at 1^0 min^{-1} for 2θ values between 20 to 90 degrees. Debye-Scherrer equation, $L = 0.9\lambda / B \cos\theta$ was used to estimate the particle size. The elemental ratio of the catalyst was derived from EDX analysis using Link ISIS EDX detector (Oxford Instruments, U.K.) attached with the scanning electron microscope. In order to determine the morphology and average particle size of the catalyst, the synthesized materials were subjected to transmission electron microscopy

(TEM) using JEOL JEM-2010 operated at an accelerating voltage of 200 kV. Specimens for the analysis were prepared by ultrasonically suspending the particles in alcohol. A drop of the suspension was deposited onto a standard carbon-coated Cu grid (GCU300, ProSciTech, Australia) and allowed to dry before being inserted into the microscope.

Experimental details of EOR analysis

The experiments were carried out at room temperature in a glass cell using a conventional three electrode set up consisting of synthesized catalysts as working electrode, Hg-HgO (MMO) as reference electrode (0.14 V vs. SHE) and bright Pt-foil (10 mm x 10 mm) as the counter electrode. The voltammetric studies on EOR were carried out in solutions containing 0.5 M NaOH and 1.0 M ethanol (AR grade, Merck, Germany) purged with nitrogen gas (XL grade, BOC India Ltd.) for 30 min at the beginning of each experiments. All the test solutions were prepared using Milli–Q water and the electrochemical experiments were carried out at room temperature.

Experimental details of ORR analysis

ORR investigations were conducted in the cathodic potential range 0.1 V to – 0.6 V, deploying the rotating disc- rotating ring disc electrode (RDE-RRDE) technique using almost the same cell set up as mentioned above, except that the working electrodes were fabricated by drop casting the synthesized catalyst ink on glassy carbon (GC) with 0.247 cm^2 area maintaining catalyst loading of 20.5 $\mu g/cm^2$ for each of the electrodes. The linear sweep voltammograms (LSV) of ORR were recorded by the help of bi-potentiostat (PINE Research instrumentation Inc., USA). Before starting each experiment the electrolyte containing 0.5 M NaOH was purged with oxygen gas (XL grade, BOC India Ltd.) at 1 bar pressure for 25–30 min. It is well known that ORR often gets sluggish due to poisoning by intermediate H_2O_2 formation, which hampers the sustainability of

the catalyst. In order to get insight into the mechanistic pathway (2e Vs 4e ORR), % H_2O_2 was estimated by deploying RRDE technique.

Chronoamperometry Study

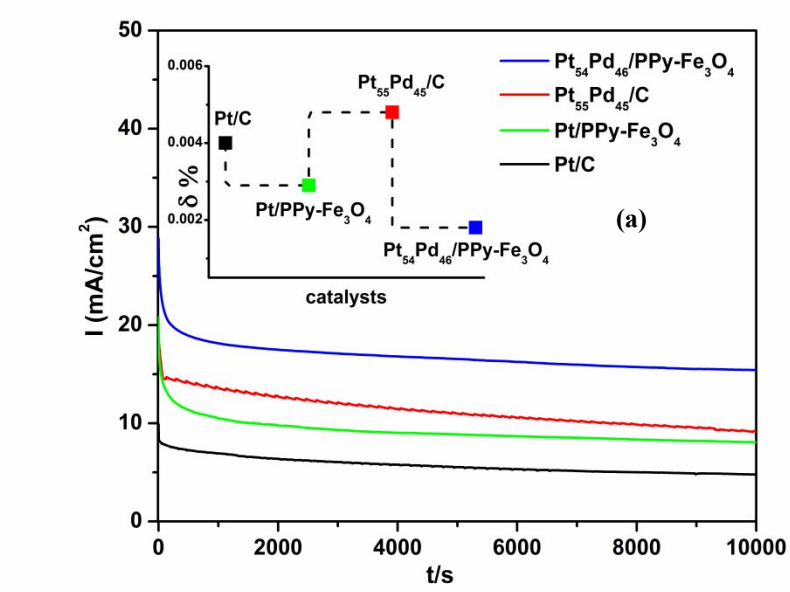

Figure.S1 Chronoamperograms recorded for the catalyst regime for 10000 seconds; **inset**: corresponding poisoning rate.

Table S1: Ion-chromatographic estimation of Acetate and Carbonate yield in ppm during EOR electro-catalysis

Catalysts	Acetate (ppm)	Carbonate (ppm)
Pt/C	**13.4**	**80.7**
Pt/PPy-Fe_3O_4	**65.6**	**120.2**
$Pt_{55}Pd_{45}$/C	**315.2**	**138.5**
$Pt_{54}Pd_{46}$/PPy-Fe_3O_4	**366.3**	**251.6**

LSV for ORR analysis

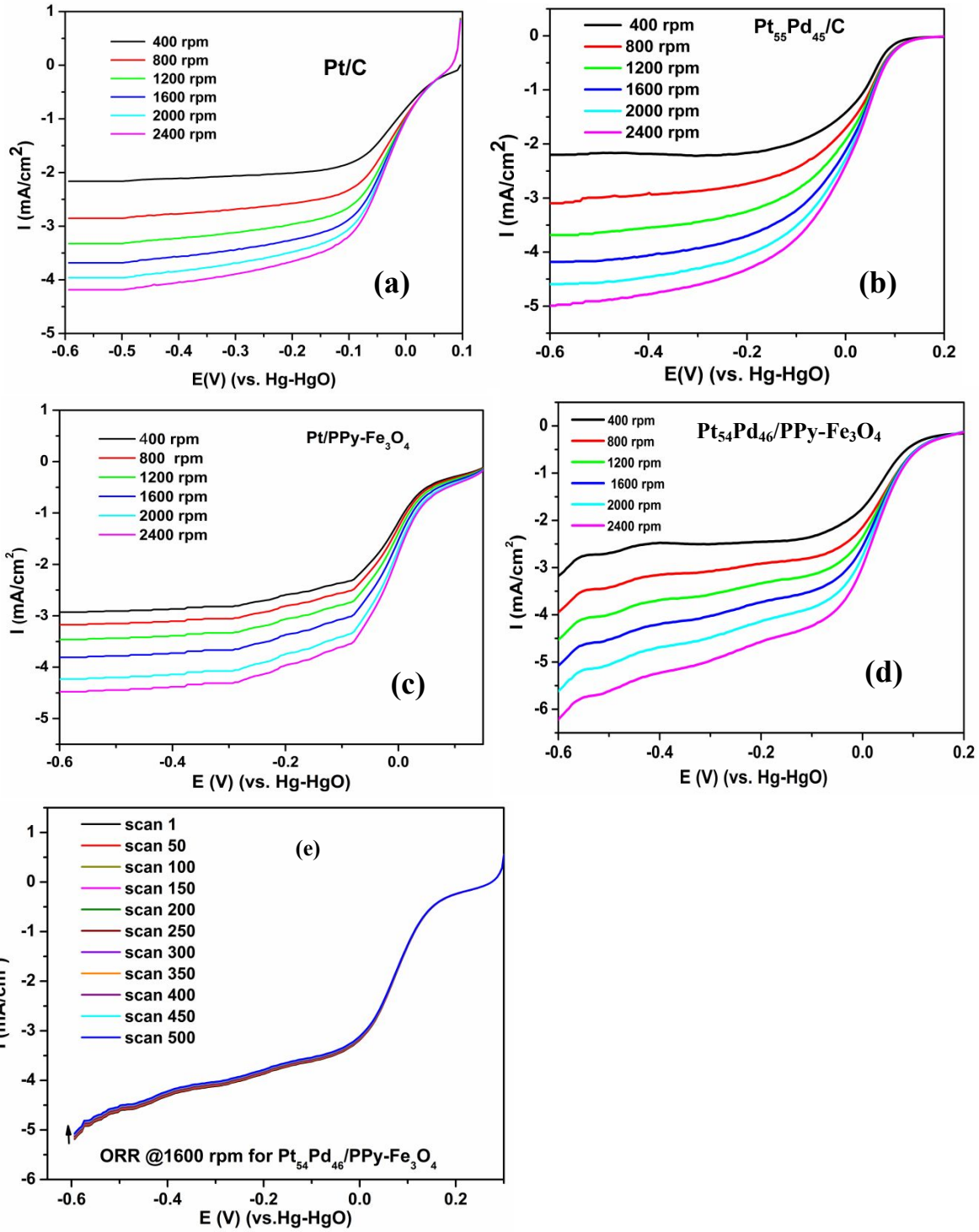

Figure S2 (a –d) linear sweep voltammograms for all the catalysts in 0.5(M) NaOH saturated with oxygen at 10mVs^{-1} scan rate at different rotation speed (400-2400rpm); (e) ORR LSV polarization study till 500 scan.

L-K characterisation & Tafel Slope for ORR study

As per Levich- Koutecky equation, for a first order reaction with respect to dissolved oxygen, the kinetic current (i_k) and the catalytic current of the disc electrode (i) are related to the rotation rate (ω) with the equation $1/i = 1/i_k + 1/(B\omega^{1/2})$,where B is the Levich slope given by: $B=0.2nF(D_{O2})^{2/3}\nu^{-1/6}C_{O2}$. Do_2 is the diffusion coefficient of oxygen in the alkaline medium, Co_2 its solubility, *v* the kinetic viscosity, n the number of electron transferred per molecule of O_2, F the faraday constant and ω the rotation rate in rpm. A plot of i^{-1} vs. $\omega^{-1/2}$ at a particular potential gives a straight line, having a slope value of B. The value of B obtained by using data for the $Do_2 = 1.63 \times 10^{-5}$ cm^{2}s^{-1}, $Co_2 = 1.03\times10^{-6}$ mol cm^{-3}, $\nu = 0.01$cm^{2}s^{-1}.

The exchange current density (i_0) was obtained by extrapolating the fitted Tafel line to where the over-potential equals zero. The slope at the relatively lower potential is due to the formation of Pt/Pd oxides and/or the adsorption of OH^- species on the electrode surface. The increment of slope at higher potential region is indicative of the reduction of oxides and/or desorption of OH^- species existing on the surface of the electro-catalysts.

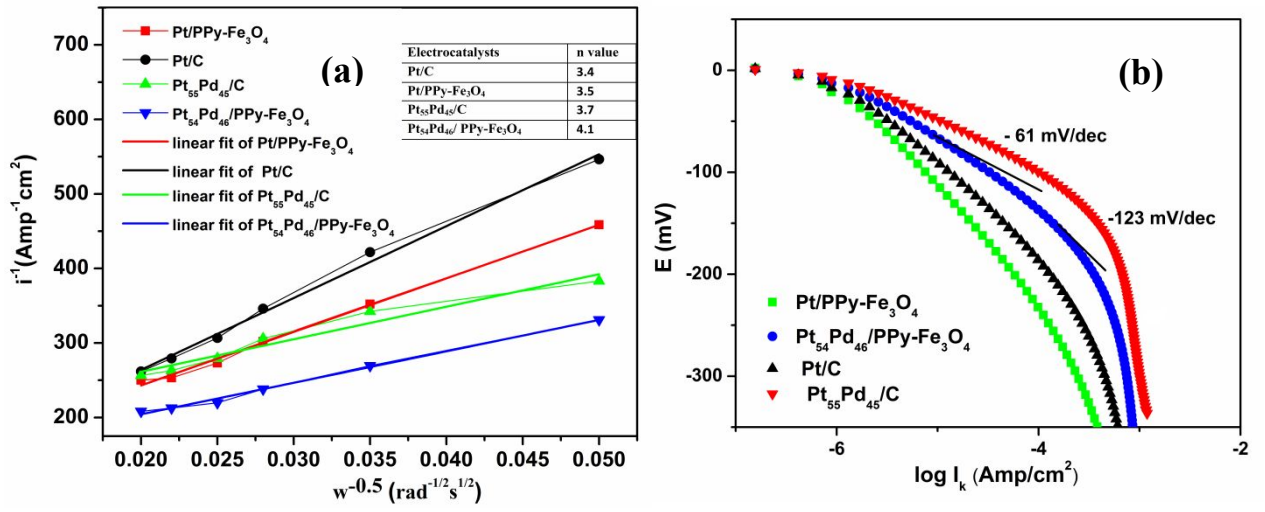

Figure S3 (a) Koutecky–Levich plot. **(b)** Mass transfer corrected Tafel plot (geometrical area normalized) at a rotation speed of 2400 rpm for all the catalysts

Table S2 ORR parameters from LSV, Tafel plot, L-K plot and H_2O_2 estimation.

Electro-catalysts	**Kinetic current density @0.05 V potential (mA/cm²)**	**Low current density**		**High current density**		**Electron exchange number (n)**	%H_2O_2 @ RRDE
		Tafel slope (B) (mV dec^{-1})	Exchange Current Density (i_0) **x 10^{-5}** A/cm²	Tafel slope (B) (mV dec^{-1})	Exchange Current Density (i_0) **x10^{-4}** A/cm²		
Pt/C	**0.44**	**–64.58**	**3.6**	**–128.67**	**6.95**	**3.4**	**6.2**
Pt/ PPy-Fe_3O_4	**0.86**	**–69.78**	**3.8**	**–141.38**	**5.90**	**3.5**	**3.8**
$Pt_{55}Pd_{45}$/C	**1.35**	**–63.13**	**6.3**	**–133.77**	**6.80**	**3.7**	**3.7**
$Pt_{54}Pd_{46}$/PPy-Fe_3O_4	**1.65**	**–61.03**	**8.2**	**–123.07**	**8.80**	**4.1**	**1.8**
PPy-Fe_3O_4	**0.015**	**–91.24**	**0.053**	**–226.39**	**0.075**	**3.1**	**8.3**

LSV and H_2O_2 estimation for the support material

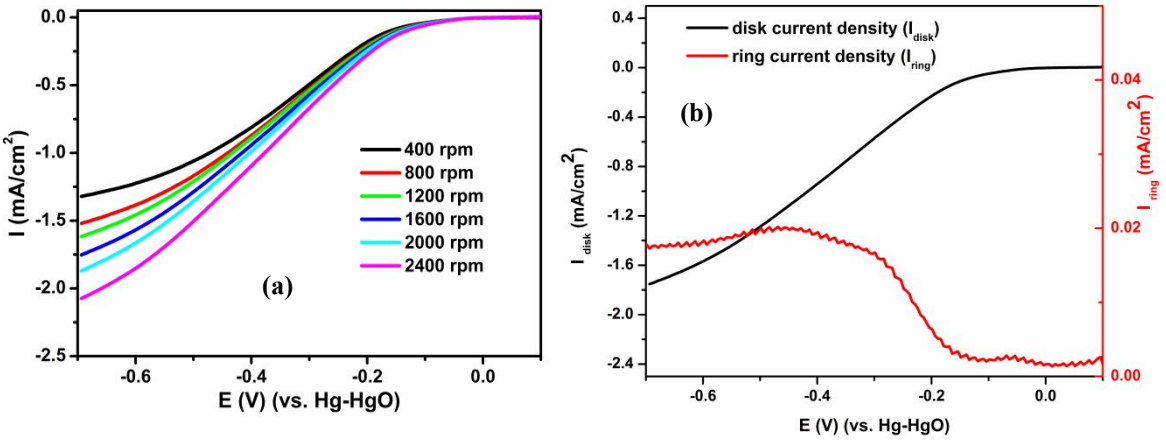

Figure S4 (a) LSVs of PPy-Fe_3O_4 in 0.5(M) NaOH at variable rotation speeds (400-2400 rpm). (b) H_2O_2 estimation of PPy-Fe_3O_4 using RRDE at 1600 rpm.

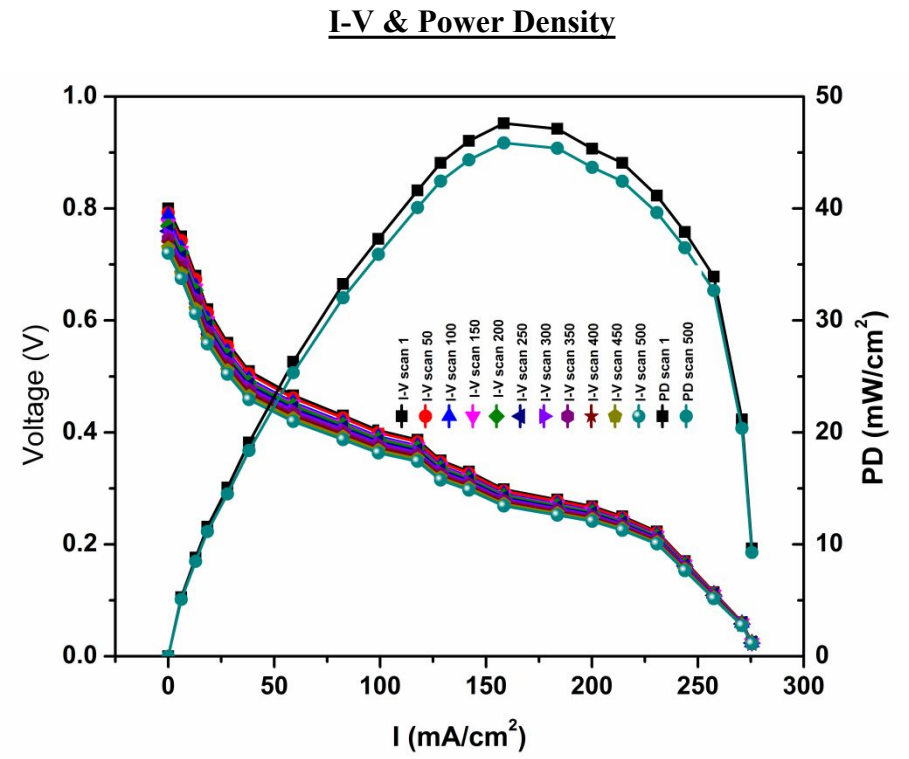

Figure S5. Polarization and power density plots for the in house fabricated DE(AEM)FC with the $Pt_{54}Pd_{46}$/PPy-Fe_3O_4 catalyst till 500 scan.