

Relationship between polypyrrole morphology and electrochemical activity towards oxygen reduction reaction

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Supporting Information

Experimental

Materials

Pyrrrole (98%) monomer (Py), iron (III) chloride (FeCl₃), and Acid Red 1 (disodium 5-(acetylamino)-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonate) (C₁₈H₁₅N₃O₈S₂·2Na) were purchased from Sigma-Aldrich. Py was vacuum distilled before use; other chemicals were used as received. The distilled Py was refrigerated and stored in the dark.

The aqueous solution of the electrolyte used, 0.1 M KOH, was prepared with ultrapure water (18.2 MΩ·cm resistivity at 25 °C). All gases (nitrogen, oxygen) were 99.995% purity. Nafion 117 solution (5 wt. % in a mixture of lower aliphatic alcohols and water) from Sigma-Aldrich was used to prepare the catalyst inks.

Synthesis

Two different polypyrrole morphologies, *i.e.* granular and tubular, PPy(g) and PPy(t) respectively, were synthesized by chemical oxidative polymerization with or without structuring agent in the reaction medium, according to previously published protocols.^[1, 2]

An aqueous solution of FeCl₃ (0.045 mol) dissolved in 50 ml of deionized water was added to a solution of Py (0.02 mol) in 50 ml of deionized water (FeCl₃/Py=2.25/1, molar ratio). The mixed solution was vigorously stirred for 6 h at ambient temperature to obtain PPy(g).

PPy(t) was synthesized using Py, FeCl₃ as oxidant and Acid Red 1 (disodium 5-(acetylamino)-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonate) as structuring agent. Py (0.02 mol) and Acid Red 1 (0.004 mol) (Py/Acid Red 1 = 1/0.2, molar ratio) were dissolved in 30 mL deionized water

with vigorous magnetic stirring for 30 min. Then, 33.4 mL of 1M aqueous FeCl₃ solution was added dropwise into the previous solution without stirring over 2 h at 278 K. The resultant mixture was allowed to stand for 24 h.

After polymerization, the precipitate was collected by filtration and washed thoroughly with deionized water and methanol to remove the residual monomers and short oligomers, oxidants and their decomposition products. The PPy polymers were further purified by a soxhlet extraction using methanol as the solvent and dried at 40 °C for 24 hours.

The resulting powders were then placed for 2 h in a tube furnace under Ar atmosphere to remove any residual air before increasing the temperature. After that, the temperature was increased at a ramping rate of 5 °C min⁻¹ until the desired heat-treatment temperature (800 °C) was reached, held at this temperature for 2 h, followed by cooling to room temperature at a rate of -5 °C min⁻¹. The final materials were called PPy(g)/800 and PPy(t)/800.

Characterizations

The scanning electron microscopy (Hitachi S-4500) was performed on materials drop casted on doped silicon crystal.

Thermogravimetric analysis (TGA) measurements were performed for PPy(g)/800 and PPy(t)/800 samples using a Q50 TA instrument. The runs were performed in platinum crucibles, containing approximately 2.5 mg of the sample under air condition. The rate heating was 10 °C min⁻¹ from 50 to 1000 °C.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Analytical Axis Ultra DLD system using an Al K α source monochromatized at 1486.6 eV. We used a hemispheric analyzer working at pass energy of 20 eV for N 1s core level.

Electrochemical measurements

The electrochemical characterizations were conducted in a single-compartment three-electrode cell using a ring-disk electrode setup with a bipotentiostat (Model VSP Bio-Logic SAS) and rotation control unit (Princeton Applied Research Model 636). Saturated KCl calomel electrode (SCE, 0.241 V vs. NHE) and a graphite plate served as reference and counter electrode, respectively. All potentials are referenced to SCE. A rotating ring disk electrode from Pine Instruments employing a glassy carbon (GC) disk (\varnothing 5 mm, $A_{\text{disk-geom.}} = 0.1963 \text{ cm}^2$) and Pt ring ($S_{\text{ring}} = 0.110 \text{ cm}^2$) was used as the working electrode.

The catalyst inks were prepared by dispersing 10 mg of each catalyst in ethanol (370 μL), H₂O (150 μL) and 5 wt% Nafion (80 μL) mixture under sonication (1h). To produce a catalyst loading of about 425 $\mu\text{g cm}^{-2}$, a 5 μL drop was placed on GC disk and dried in air. Other catalyst loadings

i.e. $255 \mu\text{g cm}^{-2}$ and $85 \mu\text{g cm}^{-2}$ were realised by the drop coating of 3 and 1 μL respectively. A commercial Pt (40 wt.%) / Vulcan (Pt/C) catalyst ink was used for comparison. 2 μL of Pt/C ink deposited on GC produce a catalyst loading of $81.50 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. Current densities were normalized in reference to the geometric area of the GC RDE (0.1963 cm^2).

The electrolyte used in all of the studies was 0.1 M KOH, and prior to measurements the electrode was cycled in N_2 -saturated solution until steady-state cyclic voltammogram (CV) was reached. O_2 was then bubbled for 30 min to achieve saturation. Under moderate O_2 bubbling, electrochemical measurements were conducted. CVs were recorded by scanning the disk potential from 0.3 to -0.9 V vs. SCE at a scan rate of 20 mV s^{-1} , and rotating ring-disk electrode (RRDE) measurements were conducted at 5 mV s^{-1} , with a rotation speed of 800 rpm. The Pt ring was set at 0.456 V vs. SCE. Stability experiments were carried out for PPy(g)/800 and PPy(t)/800 catalysts using chronoamperometry with the electrode rotation rate fixed at 1000 rpm ($E = -0.350 \text{ V}$ vs. SCE) in O_2 -saturated 1 M KOH.

The number of transferred electrons (n) and the yield of peroxide species can be also calculated from the Eq. 1 and Eq. 2 based on RRDE measurements.^[3-5]

$$n = (4I_D) / (I_D + (I_R / N)) \quad (1)$$

$$\% (\text{peroxide species}) = 100 \times (4-n)/2 \quad (2)$$

where I_D is the faradaic current at the disk, I_R is the faradaic current at the ring. The value of the collection efficiency of the rotating-ring disk electrode was determined to be $N = 0.257$, using the reversible one-electron $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple, according to the manufacturer's instructions.

References:

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Results and discussions

The morphologies and chemical compositions were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The electrocatalytic

performances towards the ORR in alkaline media according to their morphologies were studied by voltamperometry rotating ring-disk electrode (RRDE) measurements.

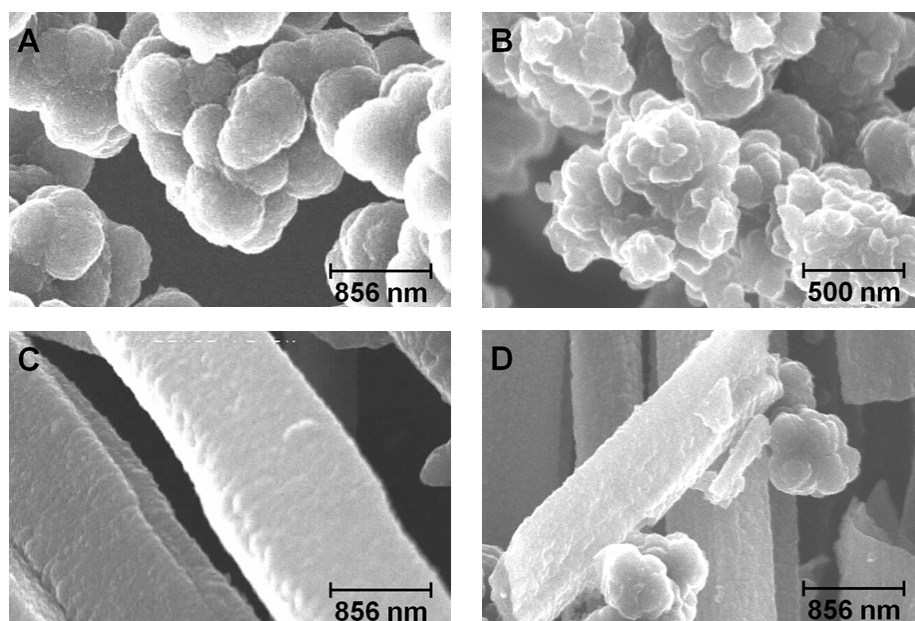


Figure S1. SEM images of PPy (g) (A), PPy (g)/800 (B), PPy (t) (C) and PPy (t)/800 (D).

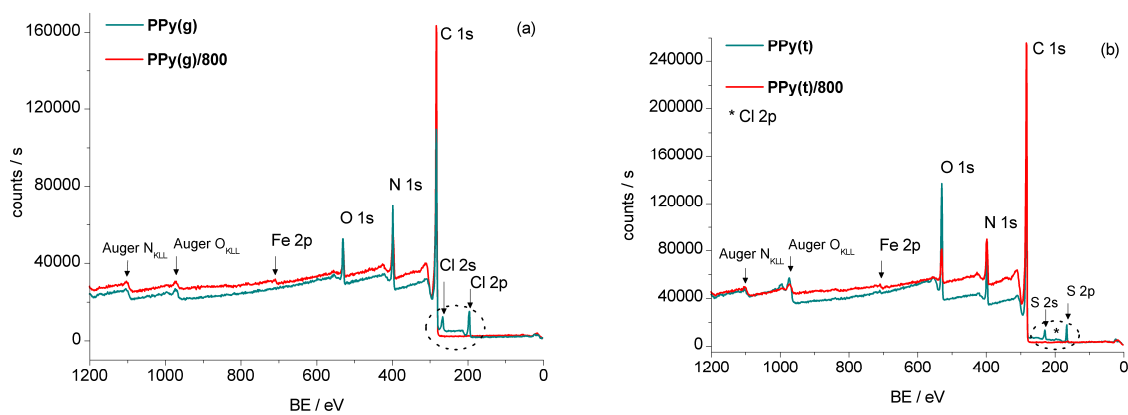


Figure S2. XPS survey spectra showing the elemental composition of (a). PPy(g) and PPy(g)/800, (b). PPy(t) and PPy(t)/800

Thermogravimetric analysis (TGA) of PPy(g)/800 and PPy(t)/800 (Fig. S3, black line) was performed under air to highlight the presence of inorganic material inside the samples. The TGA curves present only one weight-loss step between 50 and 1000 °C, for both samples. PPy polymers were fully burned within the narrow 350-600°C range. It is worth to mention that PPy(t)/800

needed a slightly higher temperature (620°C) than PPy(g)/800 (580°C) to be completely burned. For both samples, the materials remaining after annealing at 1000 °C were below 2% of the entire weight, which likely corresponds to inorganic material after purification steps.

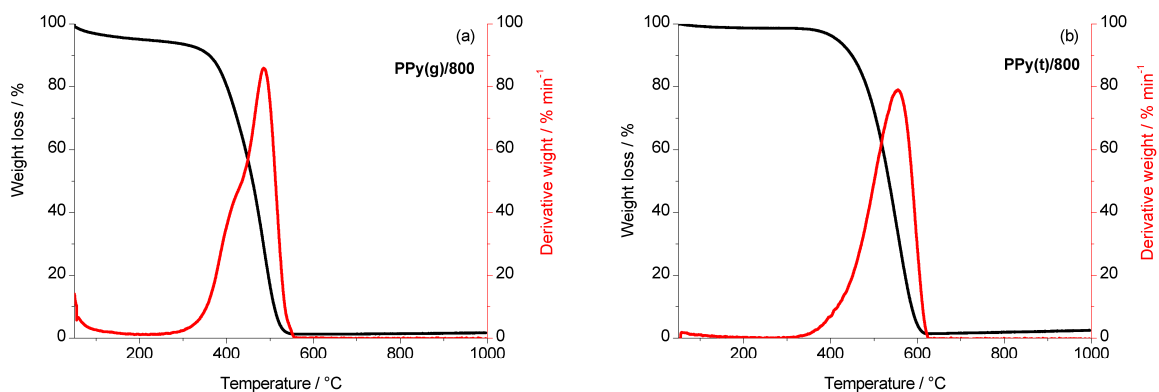


Figure S3. TGA (black) and DTG (red) curves of: (a). PPy(g)/800 and (b). PPy(t)/800

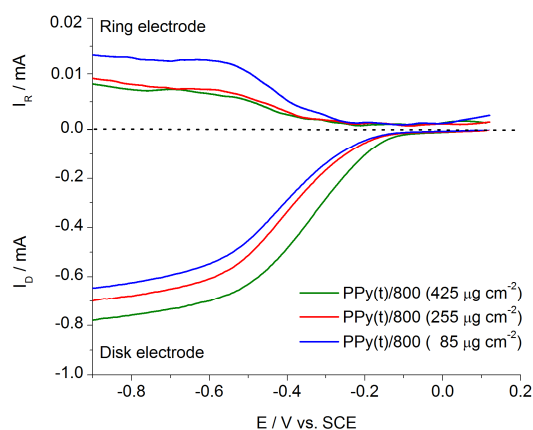


Figure S4. RRDE measurements for different loading of PPy(t)/800 in O₂-saturated 0.1 M KOH. The ring electrode was polarized at 0.456 V (5 mV s⁻¹, 800 rpm).

The impact of the PPy(t)/800 electrocatalyst loading on the ORR was investigated by RRDE experiments in 0.1 M alkaline media (Fig S4). The increase of the catalyst loading shows the formation of less peroxide species at the disk electrode. It can be explained by the the high catalyst thickness that traps peroxide species at the disk electrode and hides the compounds from the ring electrode and hides the compounds to the ring electrode. Nevertheless, the values of n found are in a narrow interval whatever the catalyst loading: 3.85, 3.82 and 3.68 for 425 $\mu\text{g cm}^{-2}$, 225 $\mu\text{g cm}^{-2}$ and 85 $\mu\text{g cm}^{-2}$, respectively. Thus, PPy(t)/800 catalysts operate under a 4e⁻ and 2e⁻ combined ORR process, with a predominant 4e⁻ pathway. Furthermore, the onset potential of the ORR is more positive for high loading.

	% C	% N	% O	% Cl	% Fe	% S
PPy(g)	71.5	17.4	6.7	4.4	-	-
PPy(g)/800	84.0	11.3	3.6	-	1.1	-
PPy(t)	67.5	12.2	16.7	0.2	0.2	3.2
PPy(t)/800	86.2	9.2	4.2	-	0.2	0.2

Peak	Component	PPy(g)		PPy(t)		Peak	Component	PPy(g)/800		PPy(t)/800	
		BE (eV)	Atomic %	BE (eV)	Atomic %			BE (eV)	Atomic %	BE (eV)	Atomic %
N1	N 1s	397.7	7.1	397.8	2.8	N5	N 1s	398	32.1	398	32.6
N2	N 1s	399.6	61.7	399.5	58.27	N2	N 1s	399.5	6.4	399.4	6.3
N3	N 1s	400.7	24.3	400.3	31.56	N6	N 1s	400.6	57.2	400.6	57.7
N4	N 1s	402.0	6.9	401.4	7.37	N4	N 1s	403.0	4.3	401.9	3.4

PPy(g)/800									
time / h	2	4	6	8	10	12	14	16	
j / mAcm ⁻²	-0.77	-0.72	-0.70	-0.68	-0.67	-0.63	-0.60	-0.595	
% loss	-	6.5	9.1	11.7	14.9	18.2	22.1	22.7	
PPy(t)/800									
time / h	2	4	6	8	10	12	14	16	
j / mAcm ⁻²	-1.77	-1.71	-1.61	-1.55	-1.55	-1.49	-1.47	-1.45	
% loss	-	3.4	9.0	12.4	12.4	15.8	16.9	18.1	

The PPy(t)/800 catalyst exhibits a reduction current density two times higher than the PPy(g)/800 catalyst. Moreover, the current density decreases more slowly in time for the tubular catalyst.