

Artificial Muscle Reversibly Controlled by Enzyme Reactions

Guinevere Strack, Vera Bocharova, Mary A. Arugula, Marcos Pita, Jan Halánek, Evgeny Katz*

Department of Chemistry and Biomolecular Science, and NanoBio Laboratory (NABLAB),

Clarkson University, Potsdam NY 13699-5810, USA

Supporting Information

Materials

The following enzymes were obtained from Sigma-Aldrich and used without further purification: diaphorase from *Clostridium kluyveri* (Diaph; E.C. 1.8.1.4), glucose-6-phosphate dehydrogenase from *Leuconostoc mesenteroides* (G6PDH; E.C. 1.1.1.49) and laccase from *Trametes versicolor* (Lac; E.C. 1.10.3.2). D-Glucose 6-phosphate sodium salt; β -nicotinamide adenine dinucleotide sodium salt (NAD^+), $\geq 95\%$ (HPLC); β -nicotinamide adenine dinucleotide, reduced dipotassium salt (NADH); sodium perchlorate, (NaClO_4) 98%+ and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), 99.5%, were also purchased from Sigma-Aldrich and used as supplied. Potassium ferrocyanide, anhydrous, 99.8% was from T.J. Baker. Pyrrole, reagent grade, 98%, from Sigma-Aldrich was distilled at 130 °C under argon until colorless and stored at 4°C under argon. Ultrapure water (18.2 M Ω cm) from NANOpure Diamond (Barnstead) source was used in all of the experiments.

Instrumentation

Absorbance measurements were performed using a UV-2401PC/2501PC UV-visible spectrophotometer (Shimadzu, Tokyo, Japan) at 23 $\pm$ 2 °C. All optical measurements of solutions utilized a 1 mL PMMA cuvette with a path length of 1 cm.

Externally applied potentials were carried out using a Metrohm Ag|AgCl|KCl, 3 M, reference electrode and a Metrohm Pt wire counter electrode using an ECO Chemie Autolab PASTAT 10 electrochemical analyzer and the GPES 4.9 (General Purpose Electrochemical System) software package in a three electrode set-up. Open circuit potential measurements established the potential

between the reference electrode and the Ppy-modified electrode and were monitored using a digital Multimeter (RadioShack) with 0.1 mV resolution.

Sample Fabrication

Polypyrrole (Ppy) samples were prepared and used for applied potential induced actuation or redox reaction induced actuation within six to seven hours of preparation. KAPTON Polyimide tape from VWM, 1IN 36YD/ROLLSCGMS, of 25- μm thickness was prepared by removing the adhesive with acetone. A 40-nm Au coating was sputtered on to the tape using CrC-150 Sputtering system, TORR International Inc, Plasma Sciences. Subsequently, the Au/polyimide tape was cut into $1 \times 20 \text{ mm}^2$ strips and connected to an electrode holder with adhesive conductive copper tape. Ppy(ClO_4) was deposited onto the Au surface by applying a constant potential of +690 mV for 380 seconds in an aqueous solution containing 0.5 M NaClO_4 and 0.2 M pyrrole. The Au-coated surface was placed facing the Pt reference electrode for deposition and for applied potential induced actuation. The 0.5 M NaClO_4 solution was purged with Ar for 5 minutes before adding the pyrrole and purged for 5 more minutes before applying the deposition potential. The deposition current was monitored over time and used to obtain an average charge density of 1.5 C cm^{-2} after 380 seconds. The final charge density was converted to an average thickness of 8.6 μm using a conversion factor, $5.7 \mu\text{m C}^{-1} \text{ cm}^2$.¹ After deposition, the Ppy was conditioned in 0.5 M NaClO_4 by cycling at 150 mVs^{-1} from -650 mV to +800 mV vs. the Ag/AgCl reference electrode. The applied potentials were cycled 15 times, or until a stable cyclic voltammogram was achieved, followed by a one hour equilibration time to ensure consistent actuator performance. Before adding the redox species with enzymes we applied a potential of 0 mV for 30 sec to set the standard initial conditions for the Ppy-strip.

Experimental results

Figure SI-1 shows the cyclic voltammograms obtained for the Ppy-functionalized polymer strip. The shape of the cyclic voltammograms and the $E_{1/2}$ potential are typical for Ppy-modified electrodes.² Figure SI-2 shows a quasi-Nernstian dependence of the open circuit potential generated on the Ppy-modified electrode on the ratio of the oxidized/reduced mediator species. The function slope is typical for the Ppy-modified electrodes.³ Figure SI-3 shows a SEM image of the Ppy-functionalized surface with heterogeneous morphology.

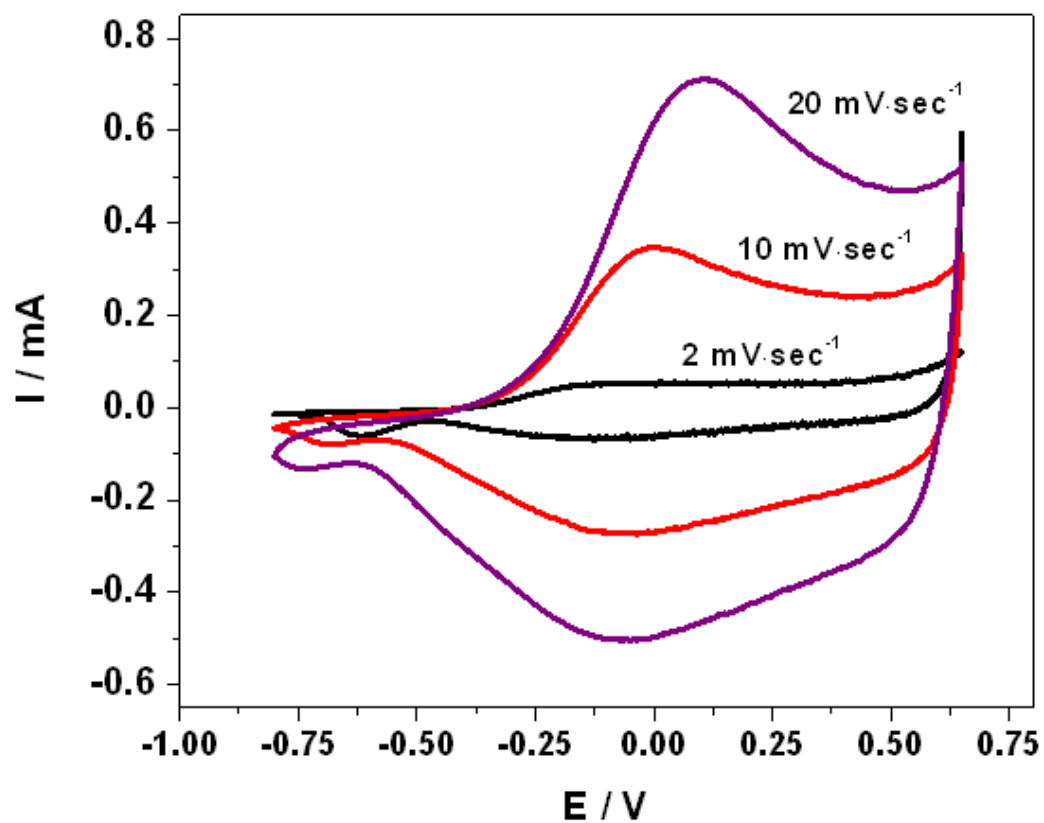


Figure SI-1. Cyclic voltammograms of the Ppy-functionalized electrode obtained at different potential scan rates in 0.5 M NaClO_4 .

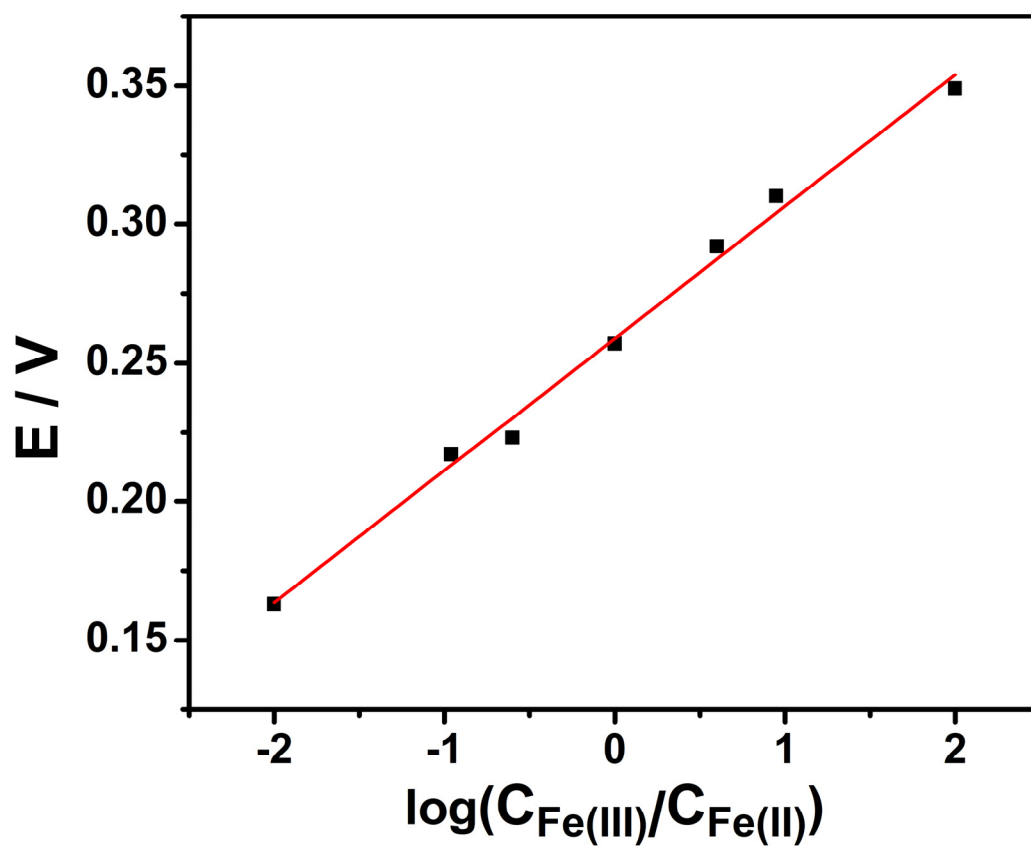


Figure SI-2. Open circuit potential generated on the Ppy-functionalized electrode in the presence of different ratios of the oxidized/reduced mediator: $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in 0.5 M NaClO_4 aqueous solution.

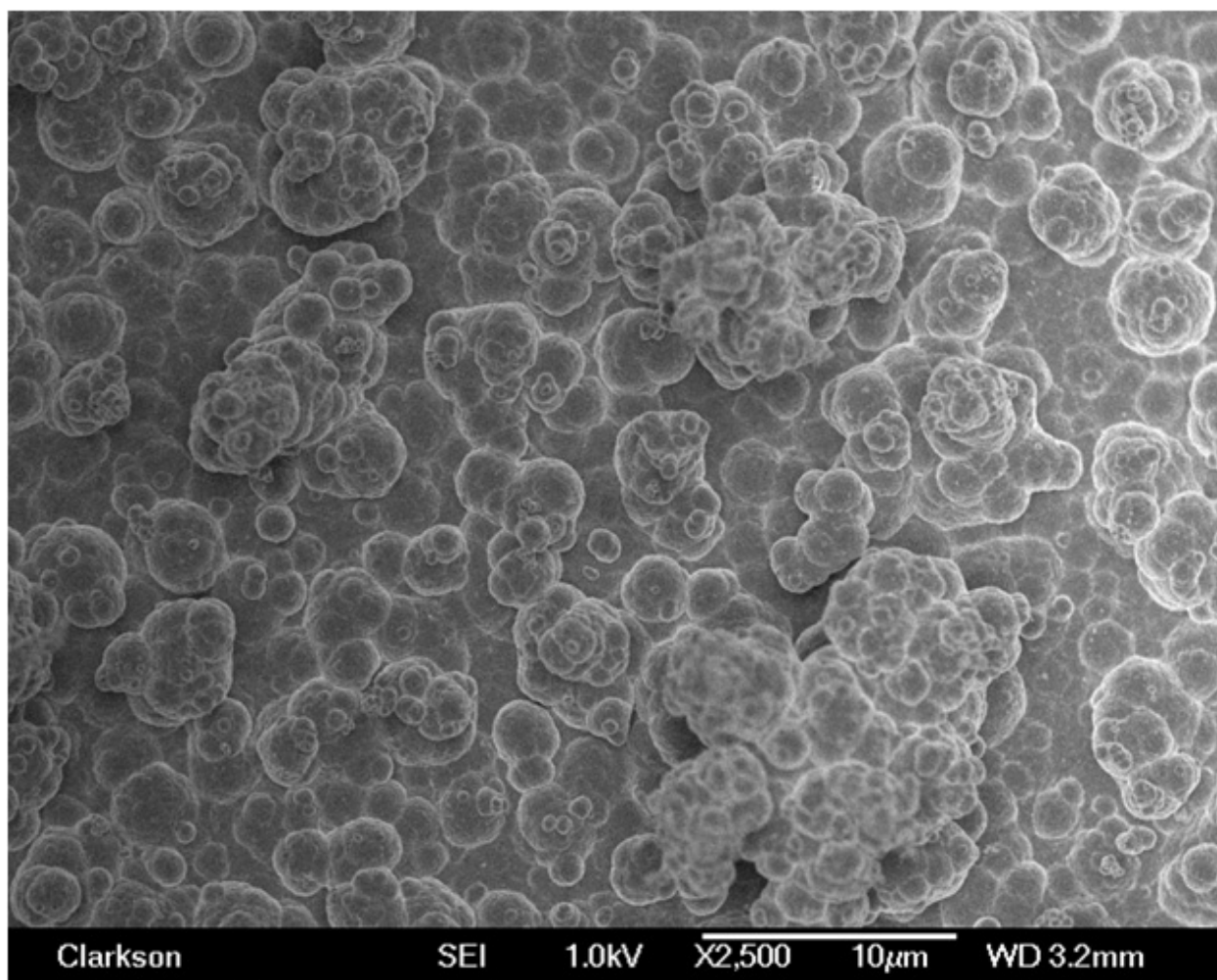


Figure SI-3. SEM image of the Ppy-functionalized surface.

References:

- (1) Krishna, V.; Ho, Y.H.; Basak, S.; Rajeshwar, K. Luminescence Probe and Voltammetry Study of Ion-Transport During Redox Switching of Poly(pyrrole) Thin-Films, *J. Am. Chem. Soc.* **1991**, *113*, 3325-3333.
- (2) Wang, L.-X.; Li, X.-G.; Yang, Y.-L. Preparation, Properties and Applications of Polypyrroles. *React. Func. Polym.* **2001**, *47*, 125-139.
- (3) Küttel, C.; Stemmer, A.; Wei, X. Strain Response of Polypyrrole Actuators Induced by Redox Agents in Solution. *Sens. Actuat. B* **2009**, *141*, 478-484.