LA-UR-15-23925
Approved for public release; distribution is unlimited.

Title:	ORR Catalyst Based on Polypyrrole Nanowires with Electrochemically Immobilized Macrocycles
Author(s):	Sansinena, Jose-Maria Chlistunoff, Jerzy Bruno
Intended for:	ECS 227th Meeting, 2015-05-24/2015-05-28 (Chicago, Illinois, United States)
Issued:	2015-05-27

ORR Catalyst Based on Polypyrrole Nanowires with Electrochemically Immobilized Macrocycles

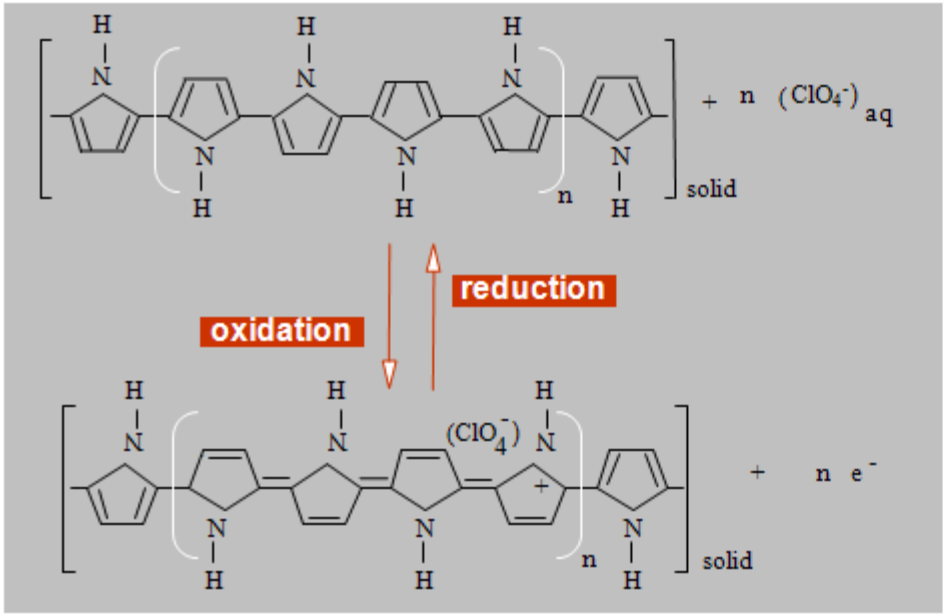
José-María Sansiñena , Jerzy Chlistunoff

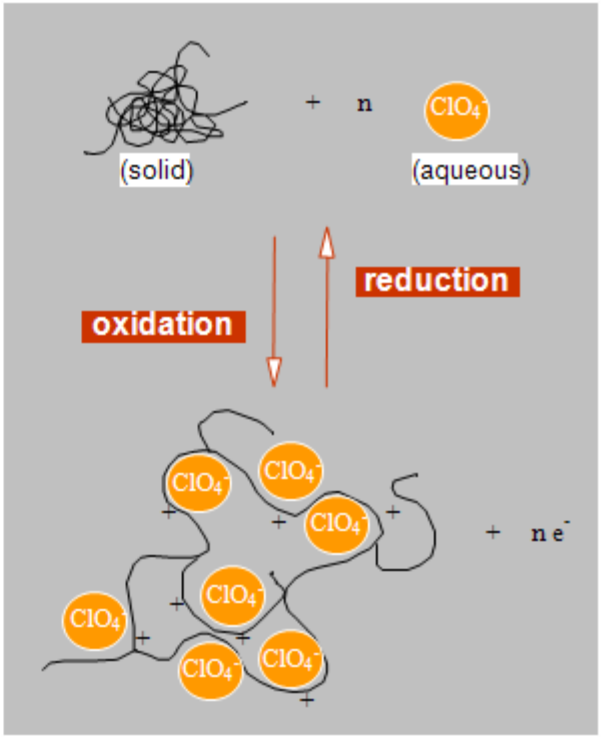
Los Alamos National Laboratory (LANL)
Los Alamos, NM 87545

May 27th, 2015

Los Alamos NATIONAL LABORATORY EST. 1943

Electrochemical oxidation/reduction of PPY

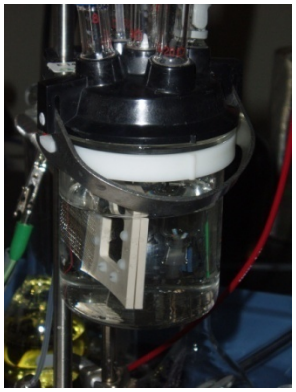




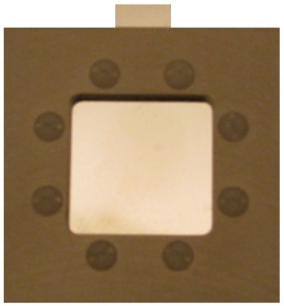
Los Alamos NATIONAL LABORATORY EST.1943

Electropolymerization of PPY

Electrochemical Cell

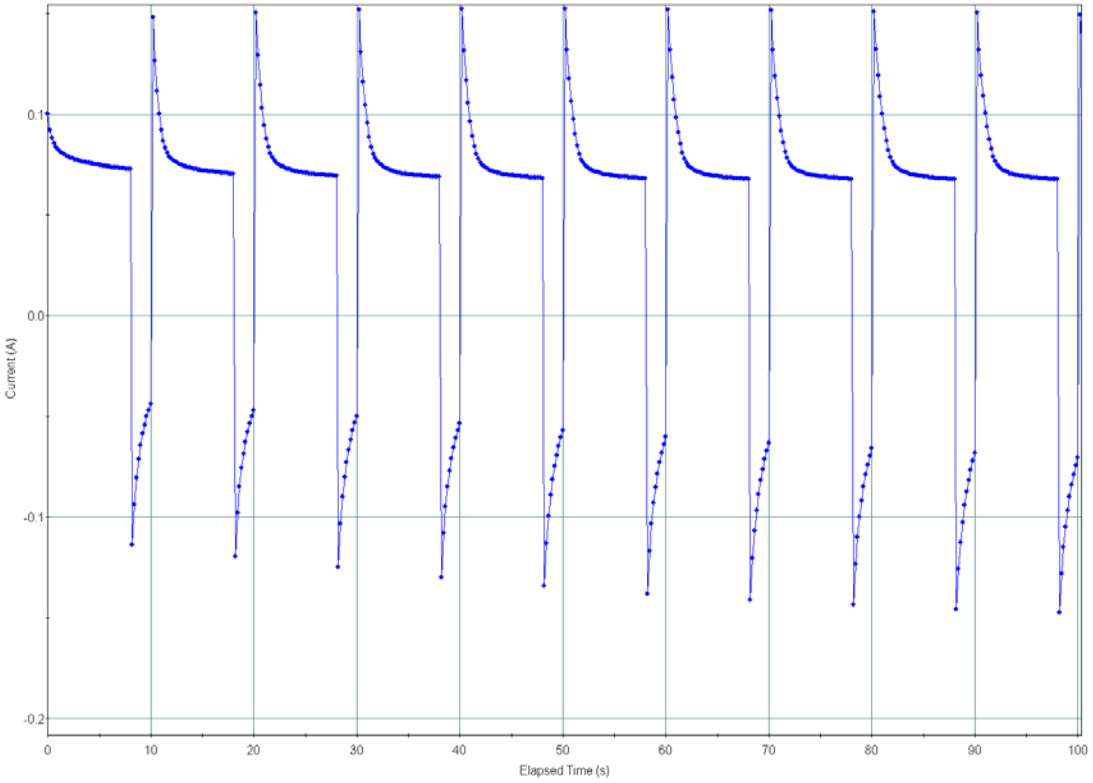


Electrode Holder



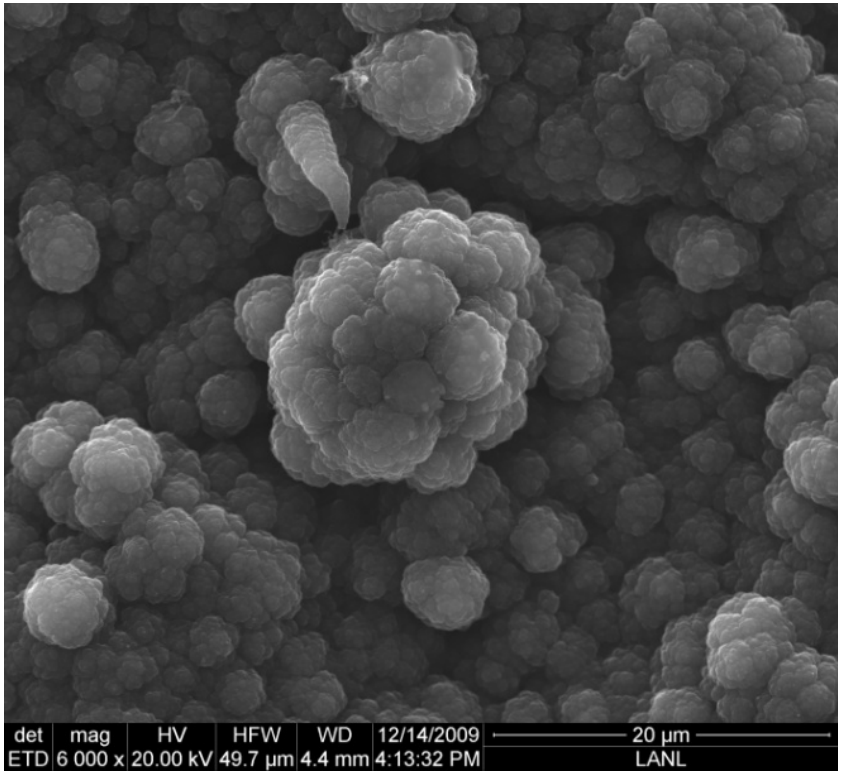
$Py + LiClO_4$

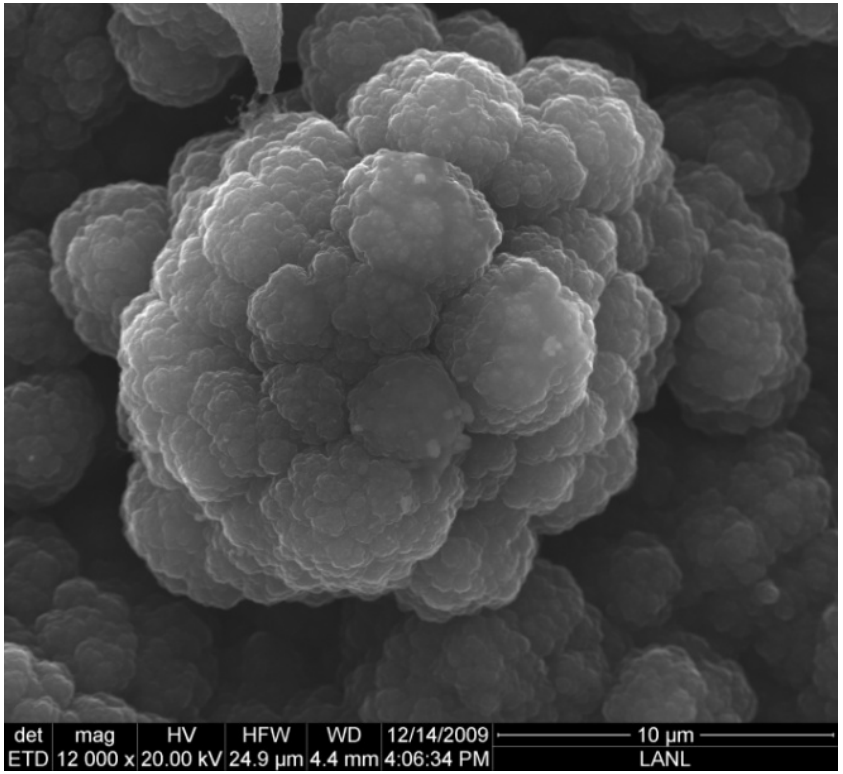
Multipotential steps
+1V (8s) / -0.1V (2s) vs RHE



Los Alamos
NATIONAL LABORATORY
EST.1943

Electropolymerization of PPY without template molecules

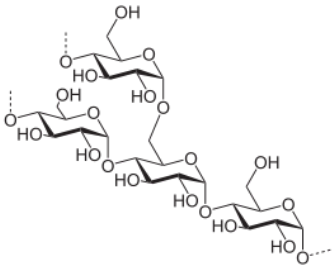




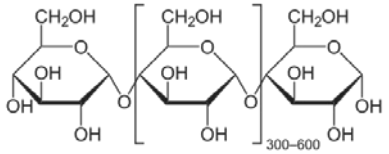
Electropolymerization of PPY nanowires using a template molecule

Search for a cheap template molecule

Starch 1g ~ less than 50 ¢



Amylopectin (75%)

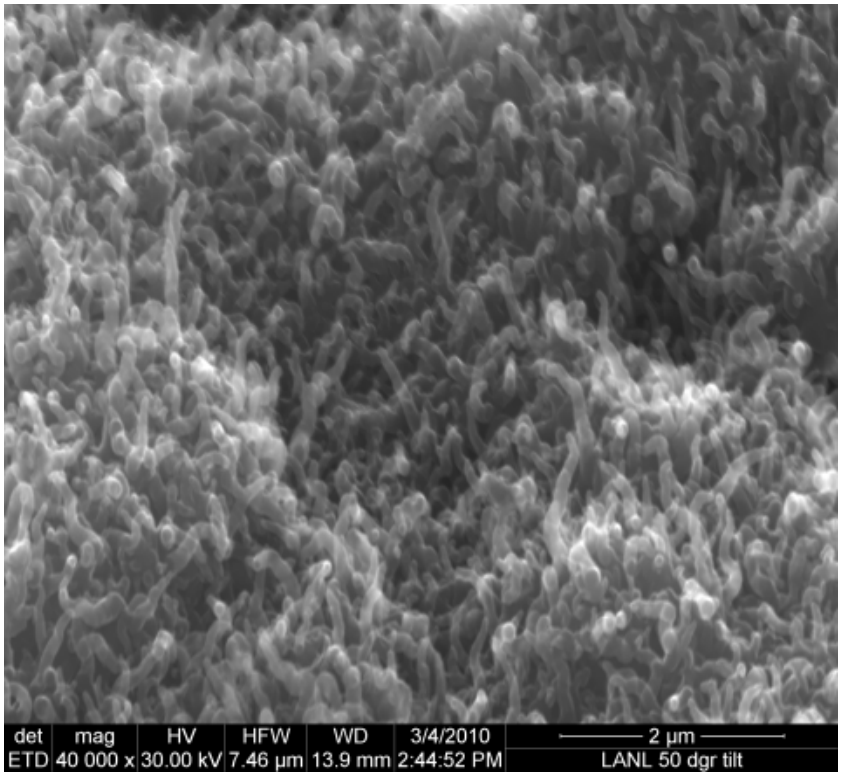


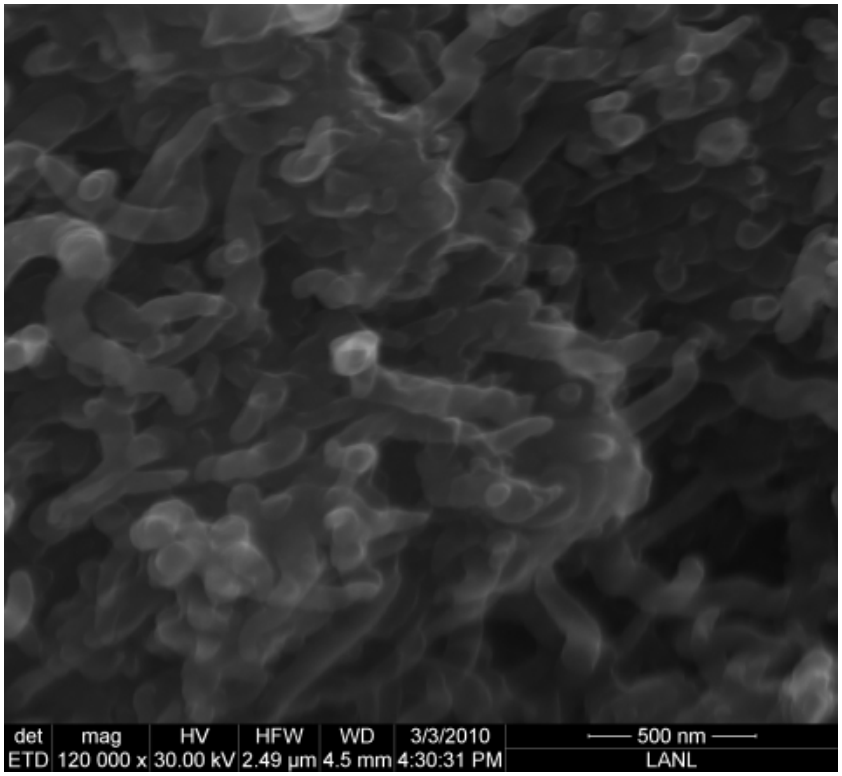
Amylose (25%)

Electropolymerization of PPY nanowires using a template molecule

PPY/starch on Graphite

Diameter ~ 75 nm



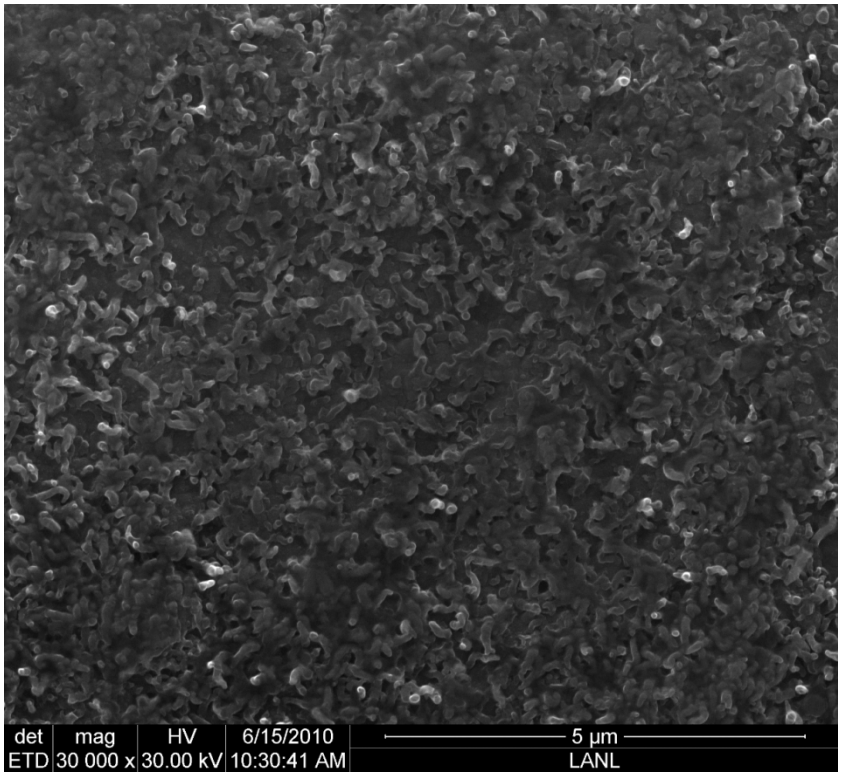


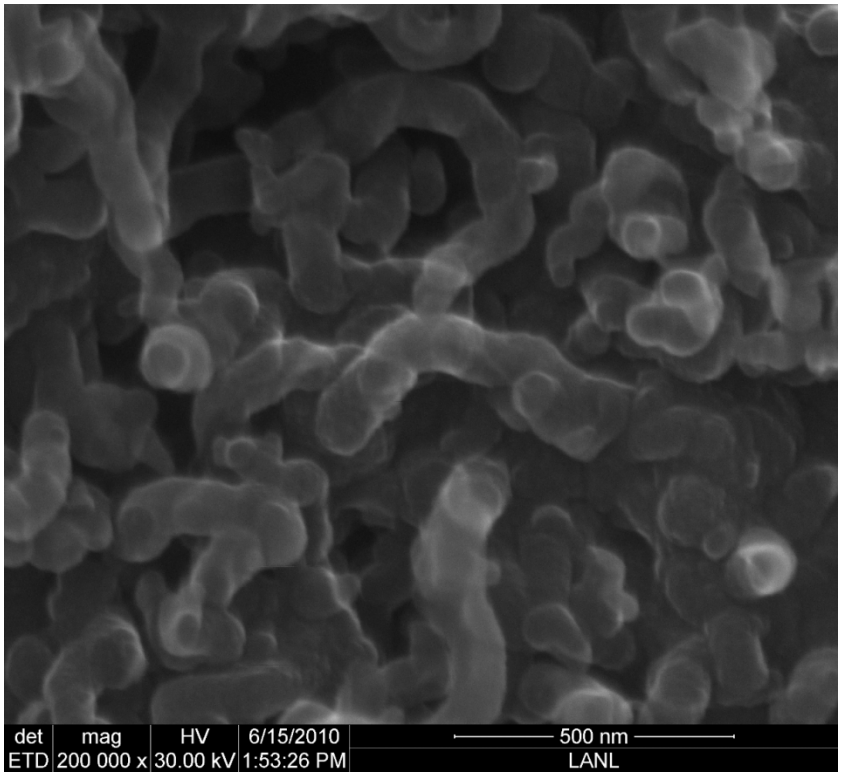
Los Alamos NATIONAL LABORATORY EST.1943

Electropolymerization of PPY nanowires using a template molecule

PPY/starch on GDL (SGL 24BC_5-23)

Diameter ~ 75 nm





Los Alamos NATIONAL LABORATORY EST.1943

Preparation of MEA's based on PPY nanowires

Approach 1:

1. Electropolymerization of PPY nanowires on solid electrodes (stainless steel, graphite, glassy carbon, etc) using template molecules (heparin, starch, etc)
2. Electrochemical or vapor deposition of Pt onto PPY nanowires
3. Transfer of PPY/Pt nanowires to a Nafion membrane by hot press to prepare a MEA

Approach 2:

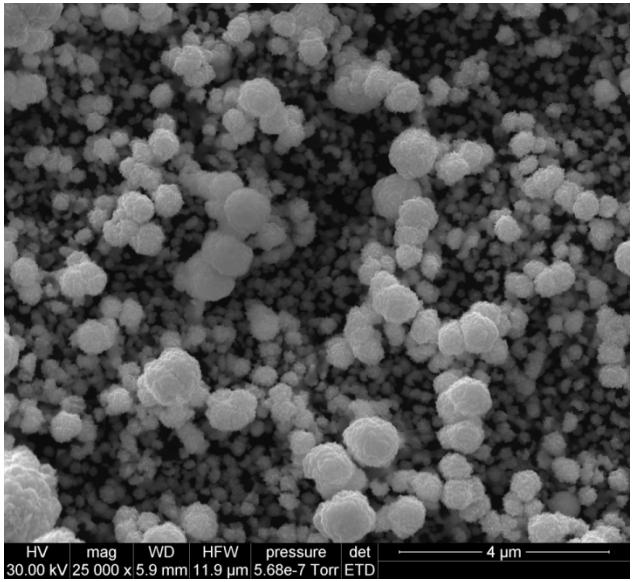
1. Electropolymerization of PPY nanowires on GDL using template molecules (heparin, starch, etc) to prepare a GDE
2. Electrochemical or vapor deposition of Pt onto PPY nanowires
3. Assembly of fuel cell using a half MEA as anode and the prepared GDE with PPY/Pt nanowires as cathode

PPY nanowires with Pt coating

Pt/PPY/starch

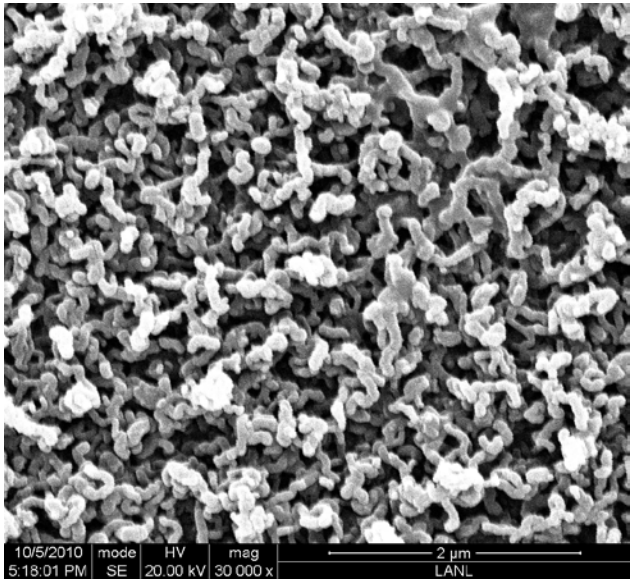
Electrochemical deposition

1wt% Na_2PtCl_6 in 0.5 M H_2SO_4 (aqueous)



Vapor deposition

(RF Magnetron Sputtering)

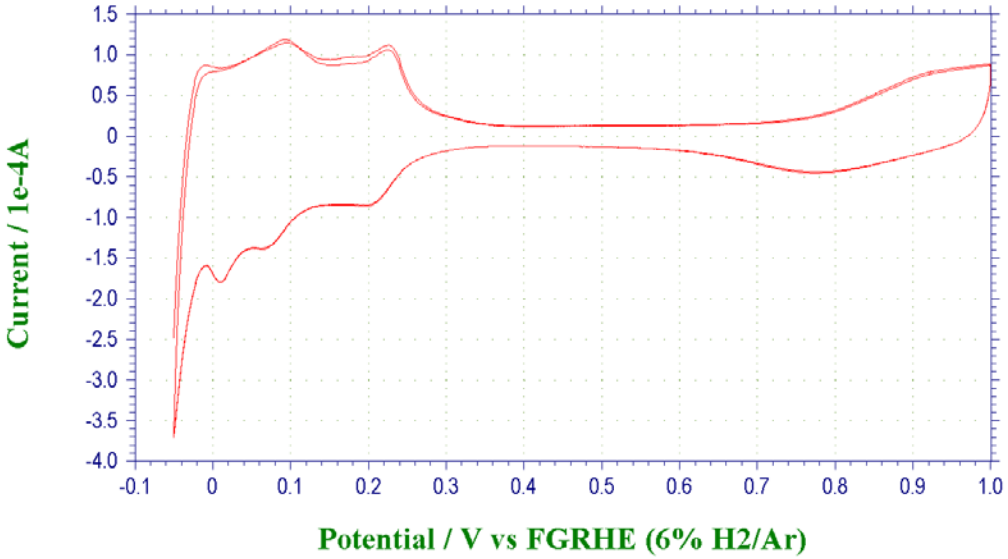


Los Alamos NATIONAL LABORATORY EST.1943

PPY nanowires with Pt coating

Qpol = 100 mC
diameter ≅ 100 nm
thickness ≅ 15 µm

Pt coated PPY/starch nanowires in 0.5M H_2SO_4



Pt loading
50 µg-cm^{-2}

Active Surface Area
14 m^2/gPt

Pt Particle Size
~ 20 nm

Los Alamos
NATIONAL LABORATORY
EST.1943

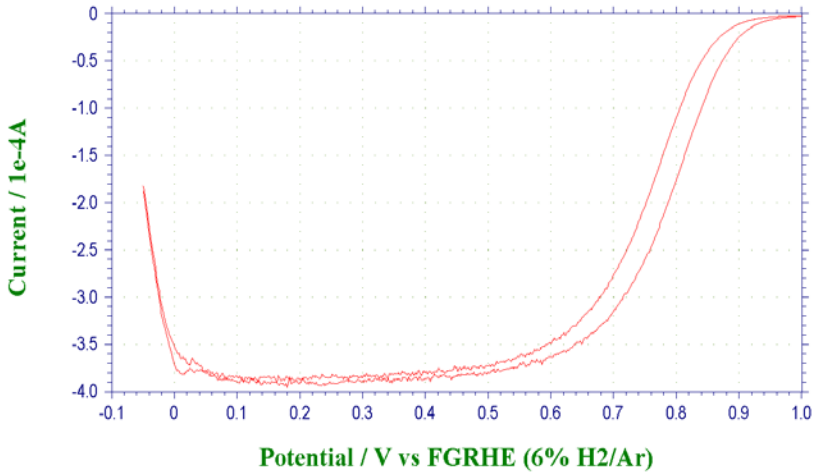
PPY nanowires with Pt coating

Qpol = 100 mC
diameter ≅ 100 nm
thickness ≅ 15 µm

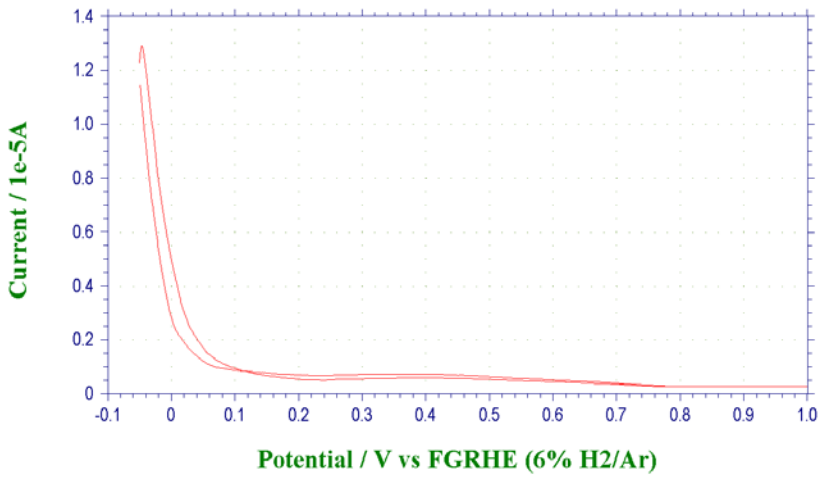
RRDE

Pt coated PPY/starch nanowires in 0.5M H_2SO_4

Disk



Ring

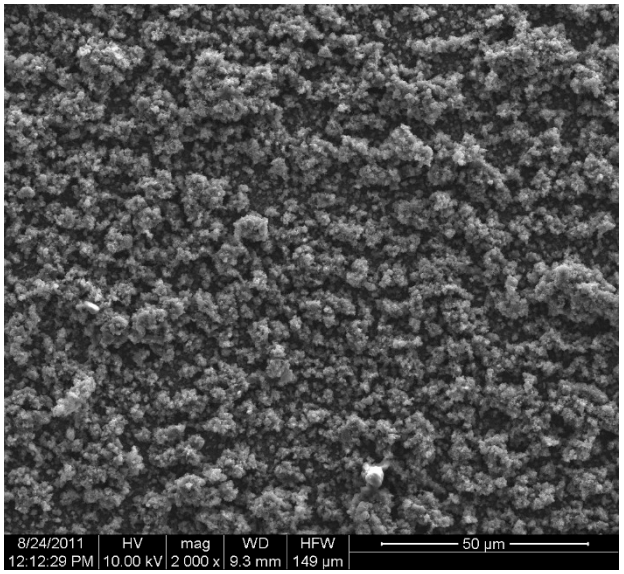


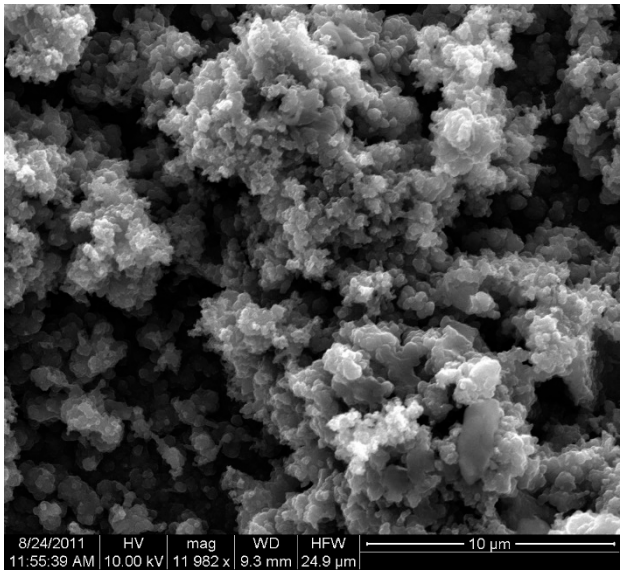
- Electrochemical synthesis of PPY nanowires was carried out on a glassy carbon (GC) disk electrode in presence of STARCH.
- Pt was deposited on PPY nanowires by vapor deposition.
- RRDE was performed in a 0.5 M H_2SO_4 aqueous solution at 400 rpm.
- XRF analysis shows a Pt loading of 50 µg.cm^2.
- ORR onset potential: 0.95 V ; ORR half wave potential: 0.80 V

Los Alamos NATIONAL LABORATORY EST.1943

PPY nanowires with Co-TPPS

PPY nanowires electropolymerized in presence of cobalt(III)- tetrakis(4-sulfonatophenyl)porphyrin (Co-TPPS)





- **Uniform electrodeposition.**
- **Open high surface area 3D structure based on PPY nanowires.**
- **Nanowires diameter ~70 nm.**

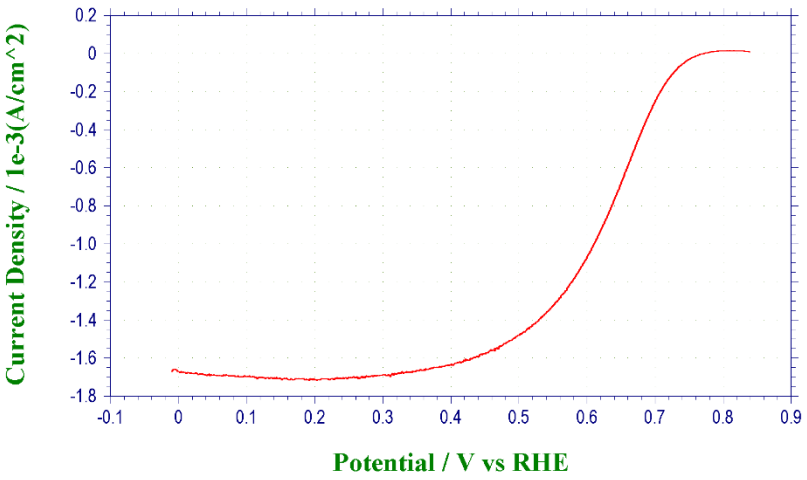
PPY nanowires with Co-TPPS

RRDE

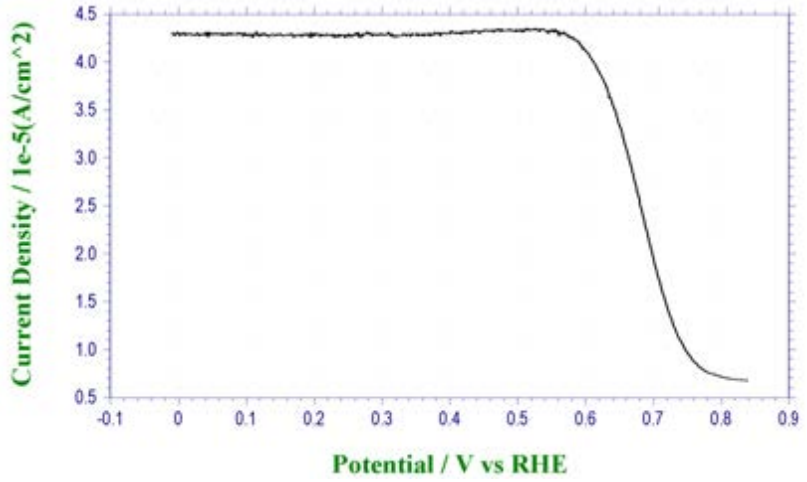
PPY/starch/Co-TPPS nanowires in 0.5M H_2SO_4

Anode: *Glassy Carbon disk, Area=0.1963 cm²* ; ***Cathode:*** *Glassy Carbon rod* ; ***Cell:*** *RRDE glass cell*

DISK



RING



- **Electrochemical synthesis of PPY nanowires was carried out on a glassy carbon (GC) disk electrode in presence of Co-TPPS.**
- **RRDE was performed in a 0.5 M H_2SO_4 aqueous solution at 400 rpm.**
- **XRF analysis shows no Pt in the sample and a Co loading of 3 µg.cm².**
- **ORR onset potential: 0.78 V ; ORR half wave potential: 0.64 V**

Los Alamos NATIONAL LABORATORY EST.1943

SUMMARY

- **PPY nanowires can be electropolymerized using STARCH as template molecule. This structure shows a conductive high surface area with the potential for enhancing both electronic conductivity and charge transport properties during ORR.**

- **Electrochemical and vapor deposition can be used for coating PPY nanowires with Pt, though the later method has shown more uniform coverage in the preliminary studies.**

- **Electrochemical polymerization of PPY / Co-TPPS nanowires as ORR catalyst can be a novel one-step electrochemical method for the direct preparation of ORR non-precious metal catalysts on a GDL.**

PPY nanowires with Co-TPPS

Future Work

- **Optimization of the direct electrochemical polymerization of PPY / Co-TPPS catalyst on a 5 cm^2 GDL for the preparation of an MEA with PPY / Co-TPPS catalyst at the cathode side.**
- **Fuel cell performance and durability study of the prepared MEA with PPY / Co-TPPS catalyst at the cathode.**

ACKNOWLEDGMENT

The financial support from the University of California Office of the President (Lab Fees Research Program Grant ID # 12-LR-237440) is gratefully acknowledged.