

Carbon-Nitrogen-Metal Material as a High Performing Oxygen Evolution Catalyst

Holly M. Fruehwald, Olena V. Zenkina, E. Bradley Easton*

Faculty of Science, Ontario Tech University (University of Ontario Institute of Technology),

2000 Simcoe Street North, Oshawa, ON, L1G 0C5 Canada

*Corresponding author: brad.easton@uoit.ca

Experimental

Chemicals

Nickel (II) chloride hexahydrate, isopropyl alcohol, and potassium hydroxide were purchased from Sigma Aldrich. Nafion® was purchased from Ion Power Inc. TPG-H-090 Toray Paper 30% Wet Proofing Carbon fibre paper was purchased from Fuel Cell Earth LLC. Vulcan XC-72 was purchased from Cabot.

Catalyst Synthesis

The detailed synthesis of the catalysts has been published elsewhere^[1-3]. Briefly, the terpyridine (tpy) ligand was coordinated to the Vulcan carbon support using diazonium coupling chemistry where a 10 mM solution of the tpy was reacted with an equal volume of 1 M NaNO₂ and let react for 3 minutes. The resulting solution was added to ca. 800 mg of the Vulcan carbon and left stir in ambient conditions for 24 hours. After the reaction was complete the solid was vacuum filtered and washed 3 times with acetone, methanol, and deionized water before being placed in the oven to dry. The resulting V-tpy was then reacted with either a 10 mM solution of Ni²⁺ (NiCl₂ · 6H₂O), Co²⁺ (CoCl₂), or Sn²⁺ (SnCl₂) stirring for 48 hours. The resulting catalysts were vacuum filtered and washed 3 times with methanol, acetone, and water to produce V-tpy-Ni, V-

tpy-Co, and V-tpy/Sn. A portion of these materials were heat treated in a tube furnace at 700 °C under N₂ atmosphere for 2 hours.

Physical Characterization

High-Resolution Transmission Electron Microscope (HRTEM) microscopy was performed at the Canadian Centre for Electron Microscopy (also supported by NSERC and other government agencies). Thermogravimetric analysis (TGA) using a TA instruments Q600 SDT thermal analyser. The catalysts were heated using a heating rate of 5°C min⁻¹ from room temperature to 1000°C while under an air atmosphere flowing at 20 mL min⁻¹. Pore size analysis was performed using a Quantachrome NOVAe 1200 pore analyser using N₂ as an adsorbate. Scanning electron microscopy (SEM) measurements were obtained using a HITACHI FlexSEM 1000. The energy of the beam was 5 kV with a working distance of 5 mm and a spot size of 20. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Nexa that is equipped with a monochromated Al K α (1486.7 eV) x-ray source. A Smart algorithm was used for background subtraction. X-ray diffraction (XRD) was performed with a Rigaku Ultima IV using Cu K α radiation. This was performed over 20-100° 2 θ at a step size of 0.01°. Detailed physical characterization has been previously reported in our last publication, see that work for more information^[2].

Electrochemical Characterization

The oxygen evolution reaction was studied using a carbon fibre paper electrode in 1 M KOH that was purified based on literature procedures prior to use^[4-6]. Catalyst inks were made by sonicating 10 mg of catalyst, 200 μ L deionized water, 200 μ L isopropyl alcohol, and 100 μ L Nafion[®]. 10 μ L of the catalyst was dropped onto a piece of carbon fiber paper and dried with

heat ($200 \mu\text{g cm}^{-2}$ catalyst loading). A mercury/mercury sulfate reference electrode was used, and a graphite rod was used as a counter electrode. Electrochemical impedance spectroscopy (EIS) was performed at 1.46 V vs RHE DC bias from 10,000 Hz to 0.1 Hz under a AC amplitude of 10 mV. The electrochemical measurements were performed using a Solartron Analytical 1470E potentiostat that was connected to a Solartron SI 1260 impedance/gain phase analyzer. All electrochemical measurements were run in triplicate to determine error.

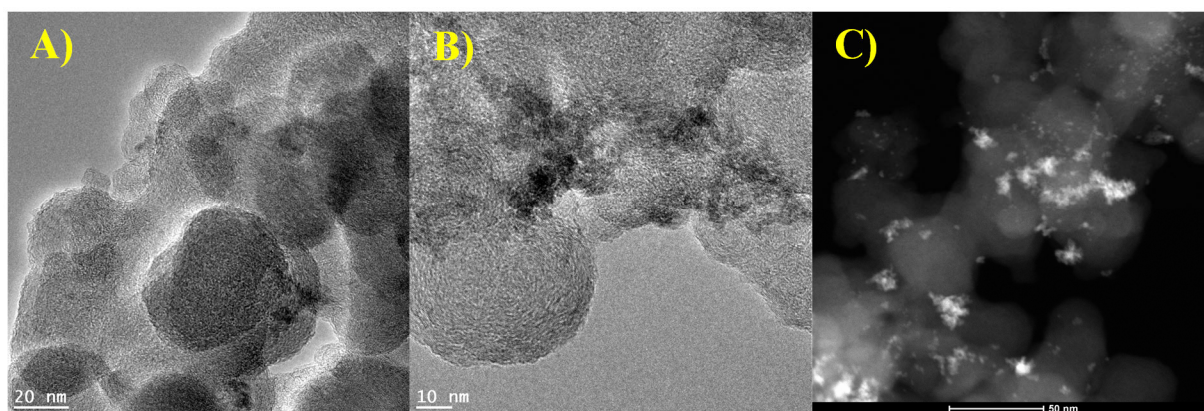


Figure S1. A-B) HRTEM images of the V-tpy/Sn catalyst C) STEM image of the V-tpy/Sn catalyst.

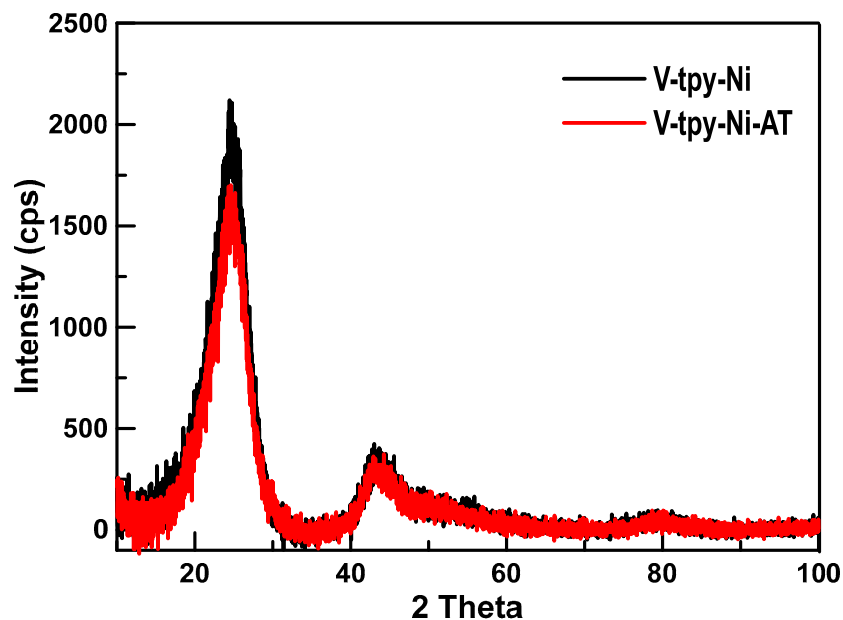


Figure S2. XRD pattern of the V-tpy-Ni and V-tpy-Ni-AT catalysts.

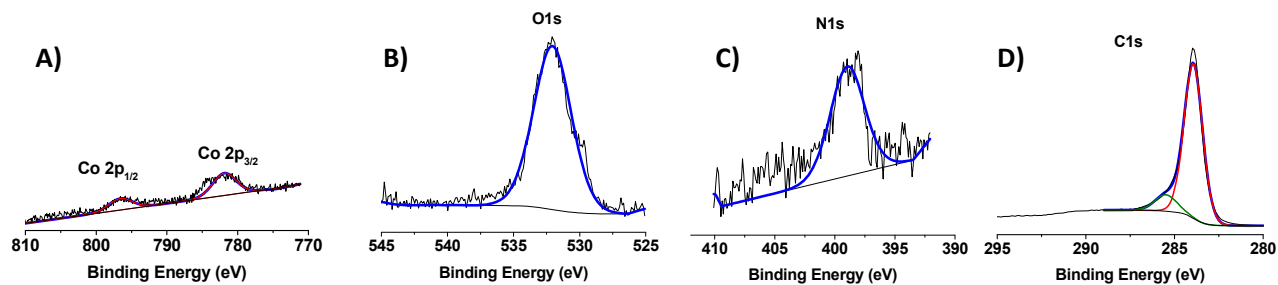


Figure S3. XPS spectra of V-tpy-Co **A)** Co 2p spectra **B)** O1s spectra **C)** N1s spectra **D)** C1s spectra.

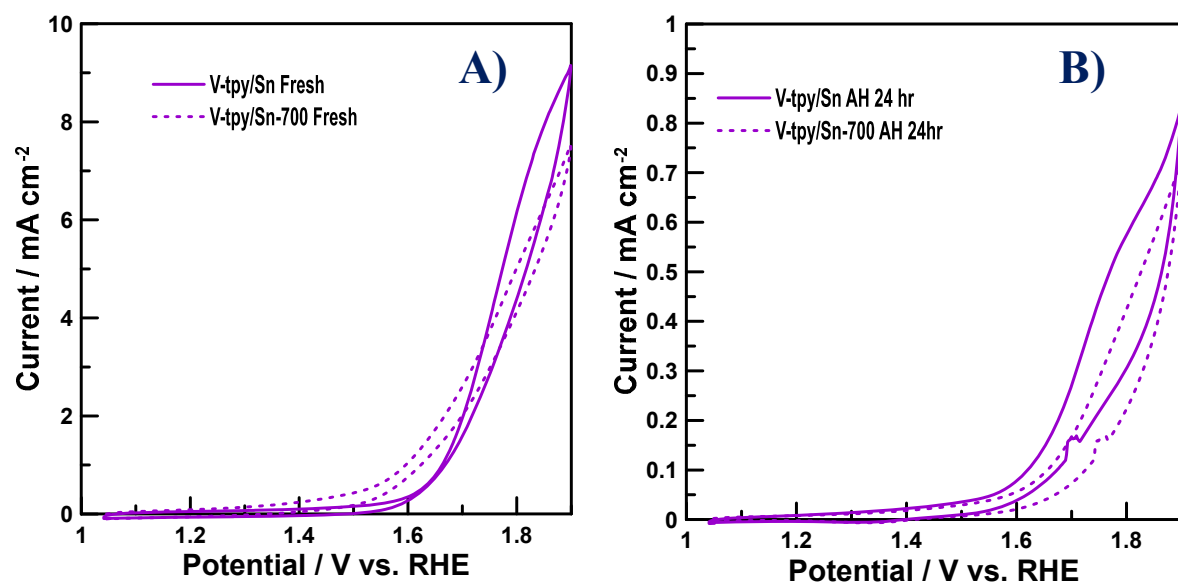


Figure S4. **A)** OER activity of the fresh V-tpy/Sn catalysts at 5 mV s^{-1} in 1 M KOH **B)** OER activity of the V-tpy/Sn catalysts after stability tests at 5 mV s^{-1} in 1 M KOH.

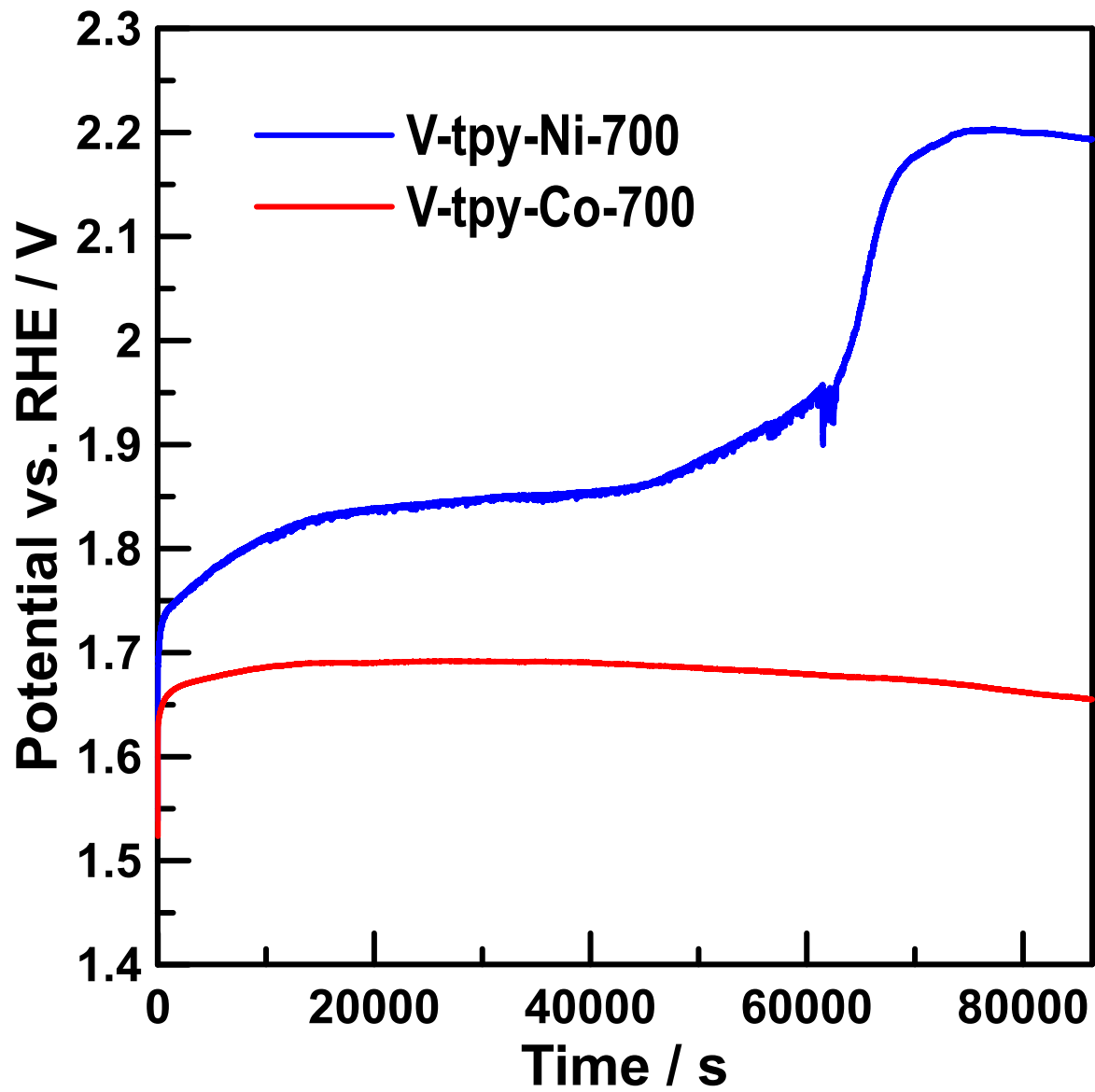


Figure S5. 24 hour galvanostatic hold at 1 mA cm^{-2} in 1 M KOH.

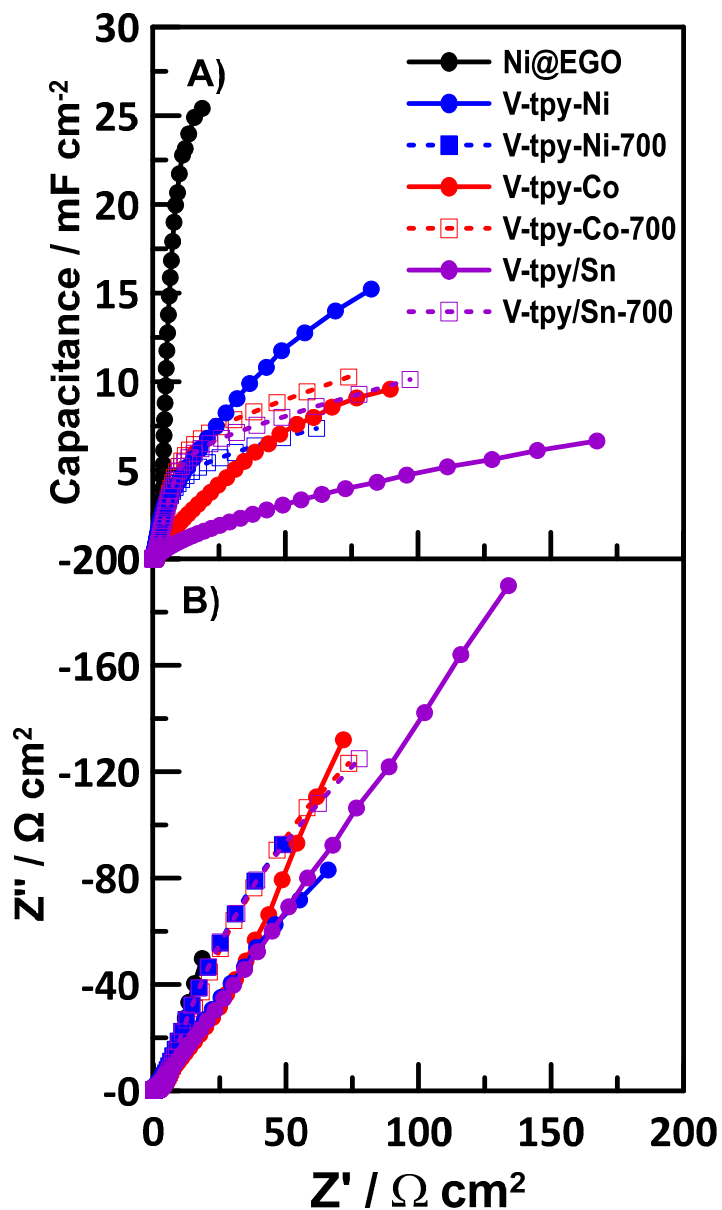


Figure S6. A) Capacitance plot of the catalysts studied in 1 M KOH B) Nyquist plot of the catalysts studied in 1 M KOH.

Table S1. Capacitance values of the catalysts tested in 1 M KOH

Catalysts	Capacitance / mF cm ⁻²
Ni@EGO	25.4
V-tpy-Ni	15.2
V-tpy-Ni-700	8.85
V-tpy-Co	9.57
V-tpy-Co-700	10.2
V-tpy/Sn	6.65
V-tpy/Sn-700	10.1

References

- [1] H. M. Fruehwald, I. I. Ebralidze, P. D. Melino, O. V. Zenkina, E. B. Easton, *J. Electrochem. Soc.* **2020**, *167*, 084520.
- [2] H. M. Fruehwald, I. I. Ebralidze, O. V. Zenkina, E. B. Easton, *ChemElectroChem* **2020**, *8*, 53-61.
- [3] H. M. Fruehwald, O. V. Zenkina, E. B. Easton, *ECS Transactions* **2019**, *92*, 523-532.
- [4] L. Trotochaud, J. K. Ranney, K. N. Williams, S. W. Boettcher, *J. Am. Chem. Soc.* **2012**, *134*, 17253-17261.
- [5] L. Trotochaud, S. W. Boettcher, *Scripta Materialia* **2014**, *74*, 25-32.
- [6] L. Trotochaud, S. L. Young, J. K. Ranney, S. W. Boettcher, *J. Am. Chem. Soc.* **2014**, *136*, 6744-6753.