# Amorphous Cobalt-based Coordination Compounds as Heterogeneous Water Oxidation Catalysts



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### Water Oxidation Catalysts: Heterogeneous vs. Homogeneous

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^ E = 0.82 V vs. NHE at pH 7$$

#### Heterogeneous WOCs





{**CoO**<sub>6</sub>}

Nocera and co-workers, Science 2008 Park and co-workers, Nature Comm. 2015

 $\{CoO_6\}$ 

- ✓ Easier Preparation
- ✓ Easier Implementation to Devices
- $\checkmark$  Better Stability during Catalytic Process



### Our Approach: Non-oxide Coordination Compounds



• Connecting Single Co sites with N-bridging ligands to form coordination compounds

### Moving from Crystals to Amorphous Compounds

 $Co^{2+}$  +  $[Fe(CN)_5L]^{n-}$   $\rightarrow$   $Co_3[Fe(CN)_5L]_2$ 



Ligand (L)	Surface Concentration (nmol.cm <sup>-2</sup> for Co sites)		
CN <sup>-</sup>	~ 1.4		
NO	~ 2		
NH <sub>3</sub>	~ 3		
Pyridine (py)	~ 6		
Bipyridine (bpy)	~ 8		

• The key to high surface concentration is to improve the amorphous nature of WOCs.

#### Previous Research



Aksoy M., Kumar Nune S. V., Karadas F., Submitted to Inorg. Chem. 2016.

### Electrocatalytic Performance

Sample	Surface concentration (nmol/cm <sup>2</sup> )	Tafel Slope (mV/decade)	References	η for 1 mA/cm <sup>2</sup> (mV)
Co-Pi	-	60	[1]	
CoHCF	1.4	88	[2]	> 600
Co-NCN	-	122	[3]	490
Co-Fe(CN)5PVP	13.4	121	[4]	510
CoFe-bpy	6.9	99		487
CoFe-HMT	8.4	84		465
CoFe-pz	5.8	95		482

CoHCF : Cobalt hexacyanoferrate Co-Pi

: Cobalt phosphate

1. Kanan M.W., Nocera D.G., Science, 2008, 321, 1072.

2. Pintado S., Goberna-Ferrón S., Escudero-Adán E.C., Galán-Mascarós J.R., J. Am. Chem. Soc. 2013, 135, 13270.

Co-NCN : Cobaltcarbodiimide

3. Bloomfield A.J., Sheehan S.W, Collom S.L, Crabtree R.H., Anastas P.T, New J. Chem., 2014, 38, 1540.

4. Aksoy M., Kumar Nune S. V., Karadas F., Submitted to Inorg. Chem. 2016.

#### Synthetic Methodology





Mixed Metal Cyanides, M<sup>II</sup><sub>a</sub>Co(L)<sup>II</sup><sub>3-a</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>

## Characterization is the Critical Step!

#### Infrared Studies on CN stretch







- Investigation of chemical properties of Co such as coordination sphere and oxidation state before&after catalysis is essential.
- Insitu characterization.

**THANK YOU**