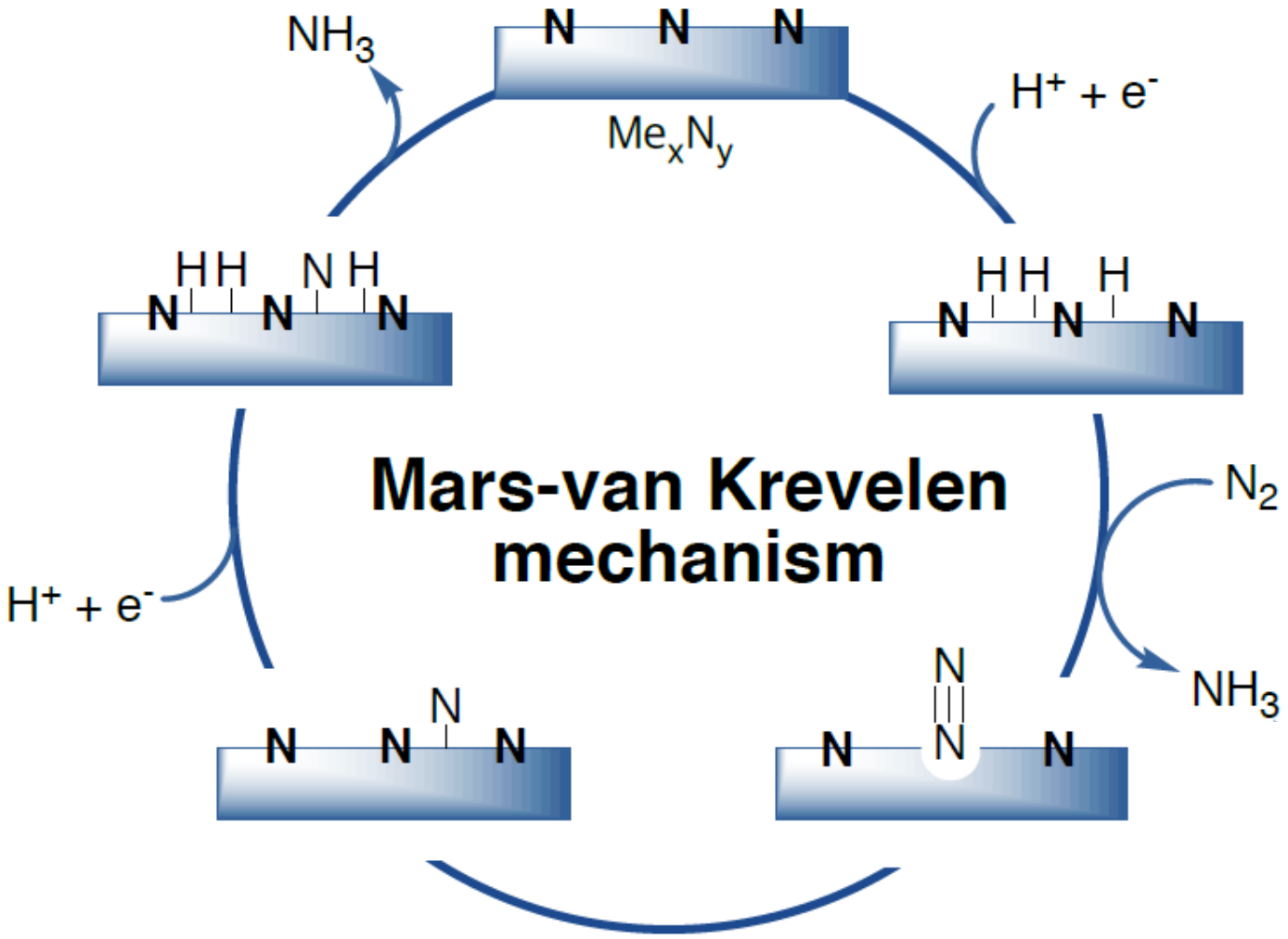
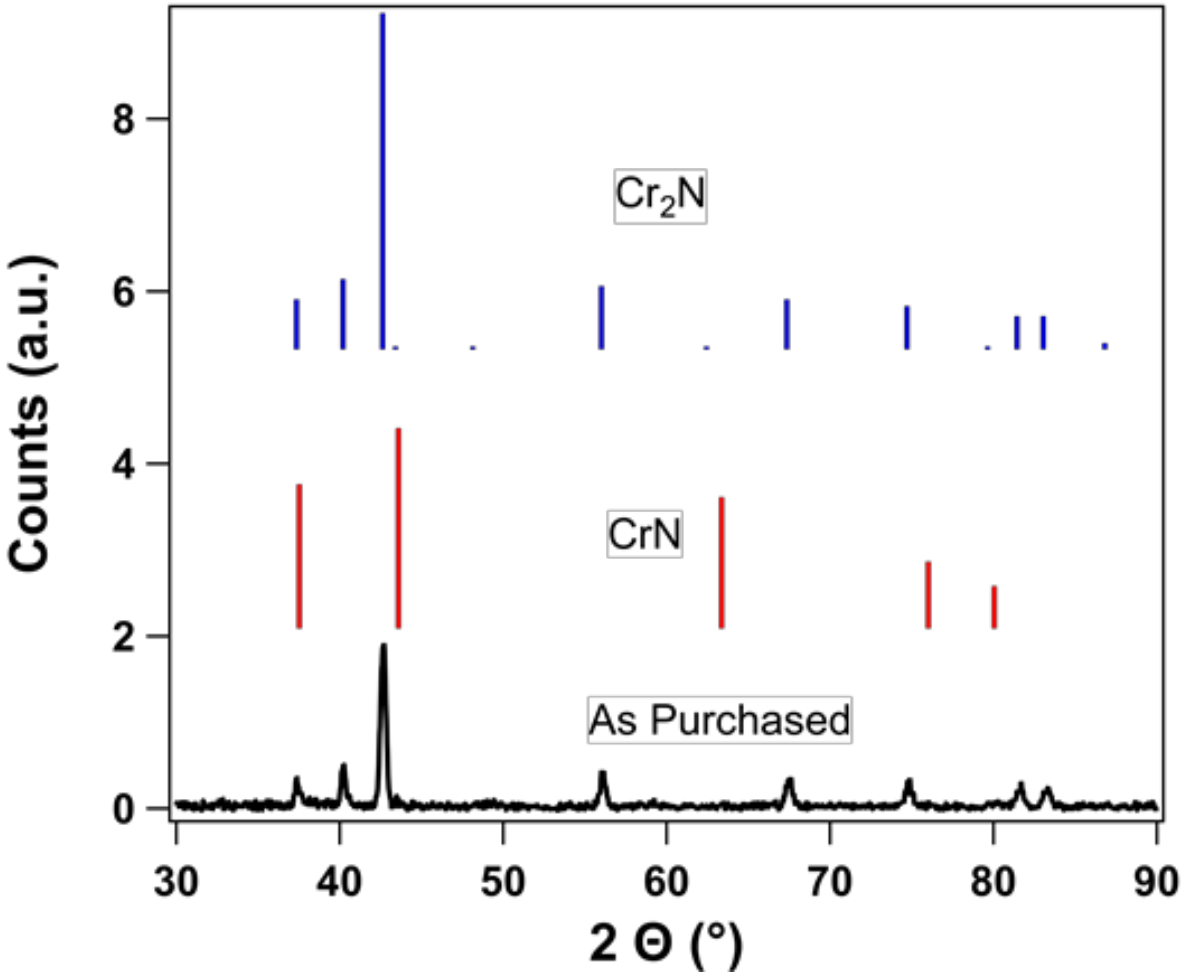
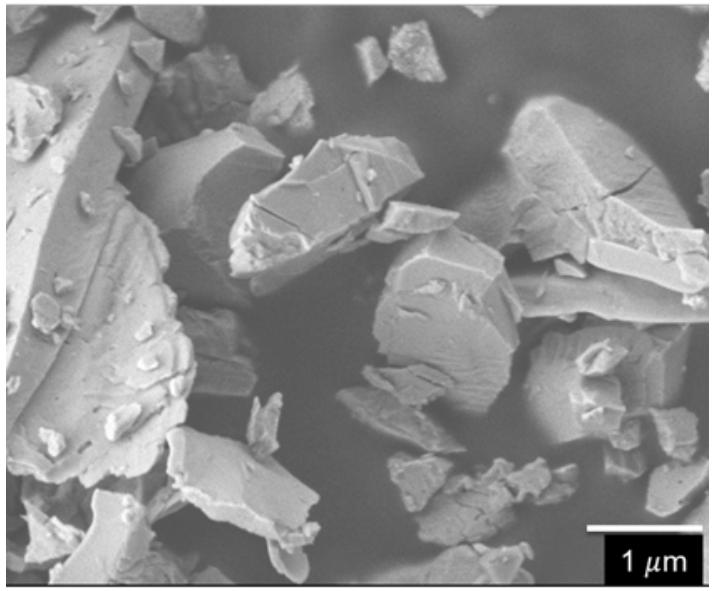
Mars-van Krevelen Mechanism for ENRR

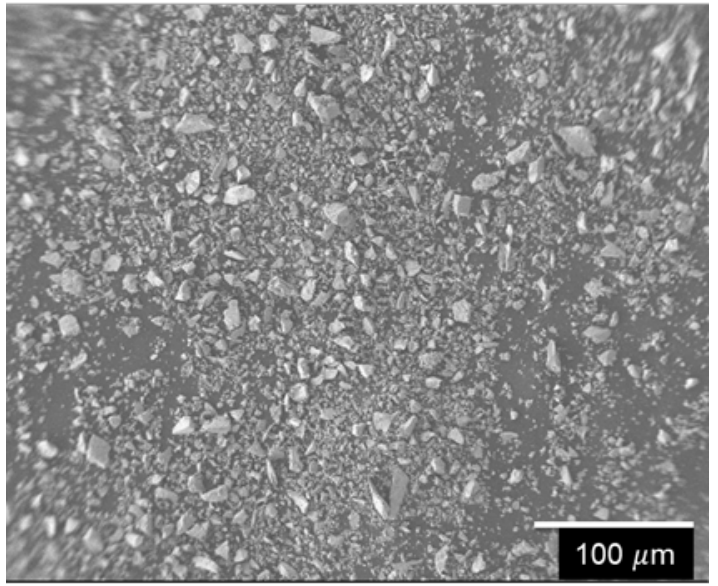


1. Abghoui Y, Garden AL, Howalt JG, Vegge T, Skúlason E. *ACS Catal* ***6, 635-646 (2016).***

Purchased Nitride Has Cr_2N Crystal Structure







- Bulk Cr_2N Crystal Structure
- Large particle sizes
  - ~3-5 μm particle size

Experimental Setup + Ammonia Analysis

Membrane Electrode Assembly

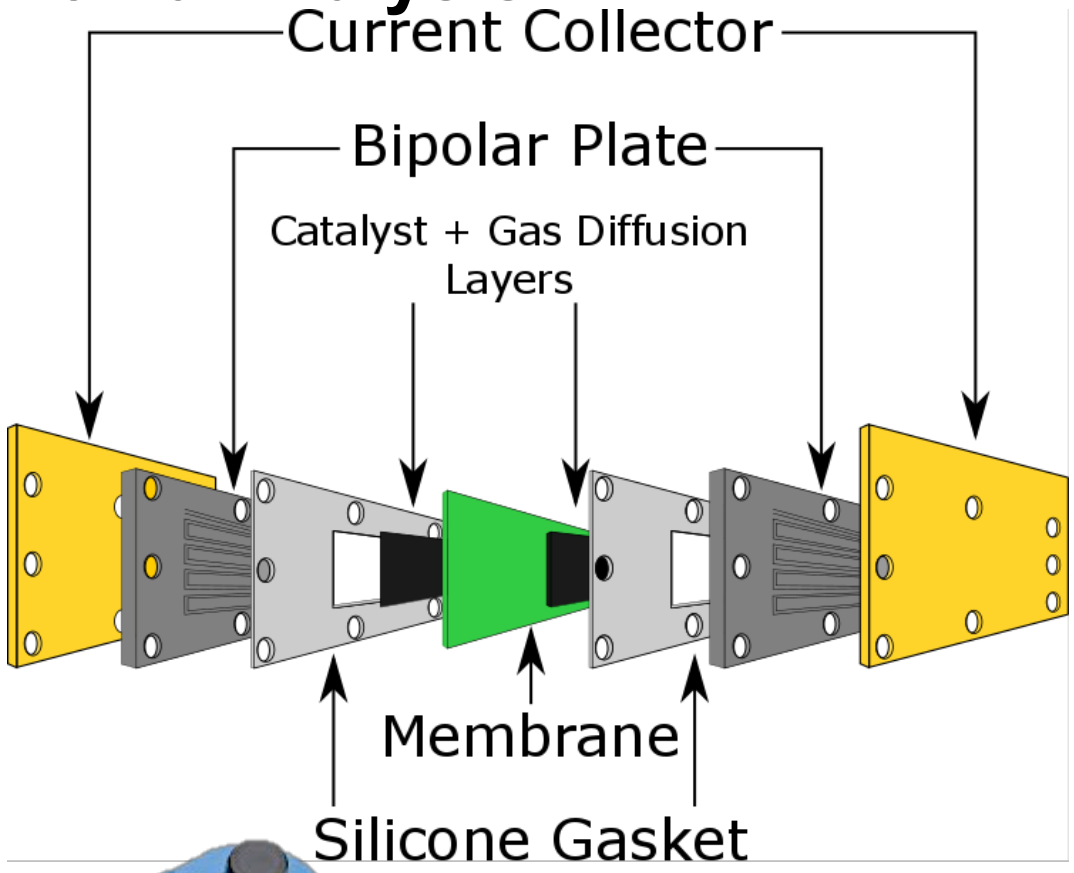
- 0.4 mg/cm^2 Pt anode
  - Counter + reference electrode
- ~1 mg/cm^2 Cr_2N loading for cathode

Testing Conditions

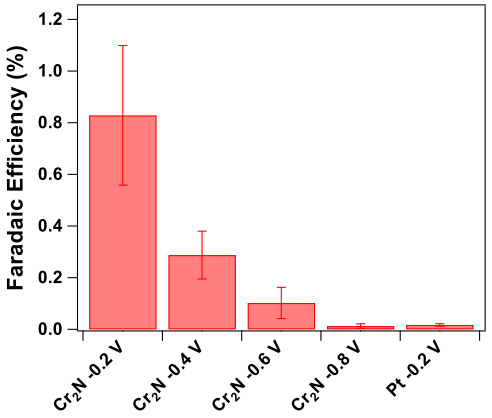
- Humidity (Cell/anode/cathode):80/85/85 °C
- Nafion 211 membrane
- Flow rates: 0.1 L/min both sides
- 24 hr tests unless noted otherwise

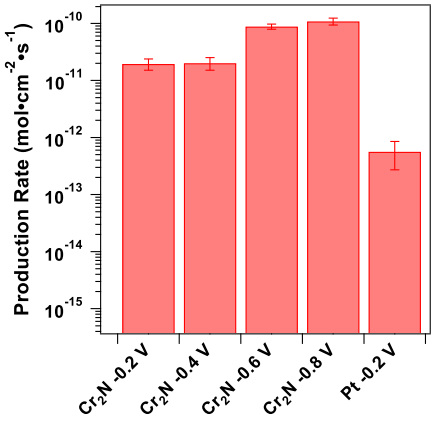
Ammonia Analysis

- Nessler's reagent colorimetric method
- Average ammonia during Ar and OCV was subtracted
  - Production rates and Faradaic efficiency's are corrected



Cr_2N Shows 50 Fold Increase in FE + Production Rate

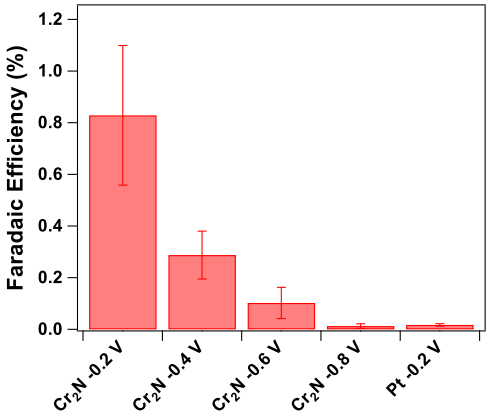


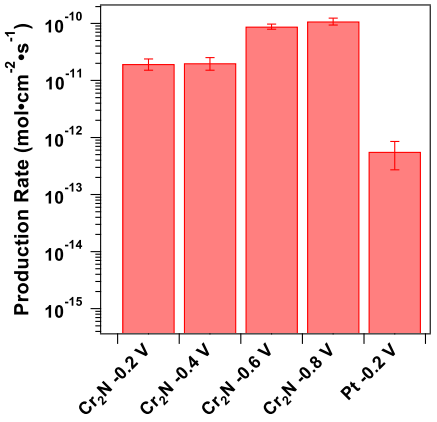


MEA Conditions:
0.4 mg/cm^2 Pt anode
1 mg/cm^2 Cr_2N cathode
0.1 L/min H_2 anode, N_2 cathode
80/85/85 ^{o}C cell, anode, cathode

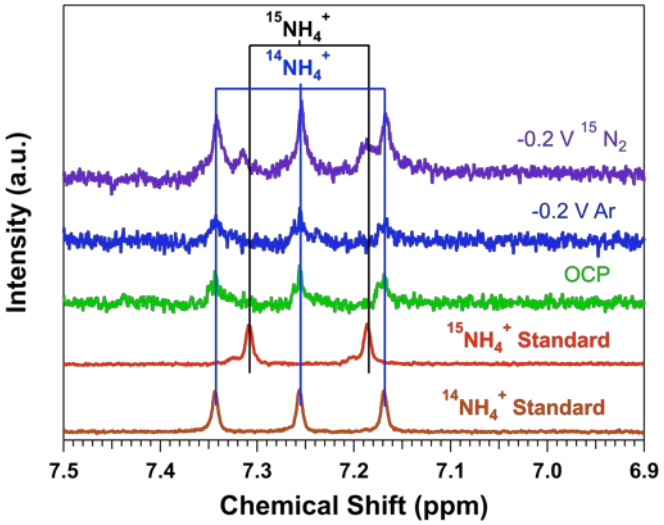
- 2 order of magnitude increase in faradaic efficiency compared to Pt at -0.2 V
  - Increasing potential favors the HER
- Specific production rates are 2 orders of magnitude higher for Cr_2N

Cr_2N Shows 50 Fold Increase in FE + Production Rate





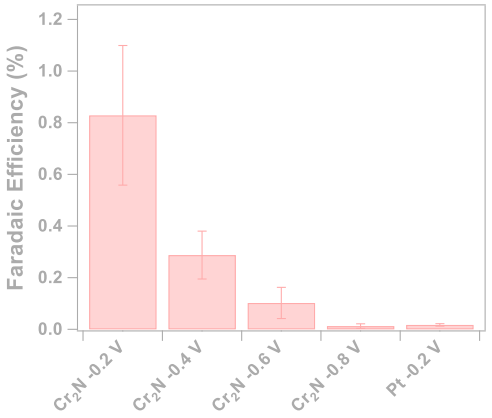
MEA Conditions:
0.4 mg/cm^2 Pt anode
1 mg/cm^2 Cr_2N cathode
0.1 L/min H_2 anode, N_2 cathode
80/85/85 ^{o}C cell, anode, cathode

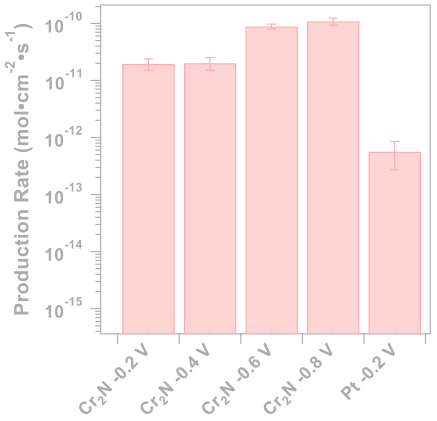


- 2 order of magnitude increase in faradaic efficiency compared to Pt at -0.2 V
  - Increasing potential favors the HER
- Specific production rates are 2 orders of magnitude higher for Cr_2N
- Batch cell with $^{15}N_2$ gas shows $^{15}NH_4^+$
  - Confirms activation of N_2 gas

Batch Conditions:
Pt counter electrode
1 mg/cm^2 Cr_2N cathode
80^{o}C cell
Sealed cell with positive pressure

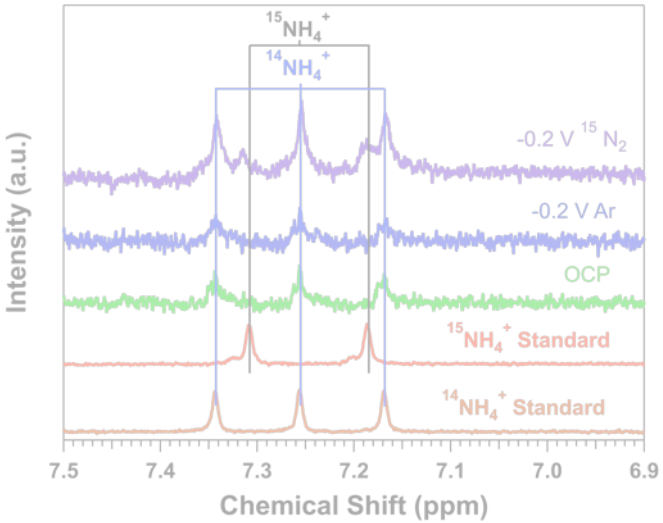
Cr_2N Shows 50 Fold Increase in FE + Production Rate





MEA Conditions:
0.4 mg/cm^2 Pt anode
1 mg/cm^2 Cr_2N cathode
0.1 L/min H_2 anode, N_2 cathode
80/85/85 ^{O}C cell, anode, cathode

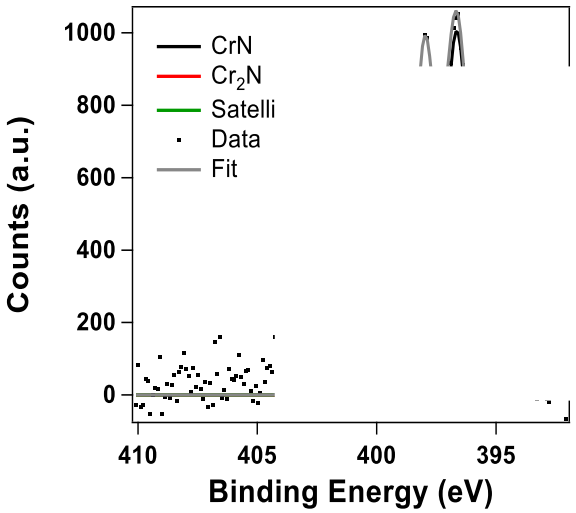
What is the surface composition?



- 2 order of magnitude increase in faradaic efficiency compared to Pt at -0.2 V
  - Increasing potential favors the HER
- Specific production rates are 2 orders of magnitude higher for Cr_2N
- Batch cell with $^{15}N_2$ gas shows $^{15}NH_4^+$
  - Confirms activation of N_2 gas

Batch Conditions:
Pt counter electrode
1 mg/cm^2 Cr_2N cathode
80^{O}C cell
Sealed cell with positive pressure

XPS Peak Assignments of Cr_2N



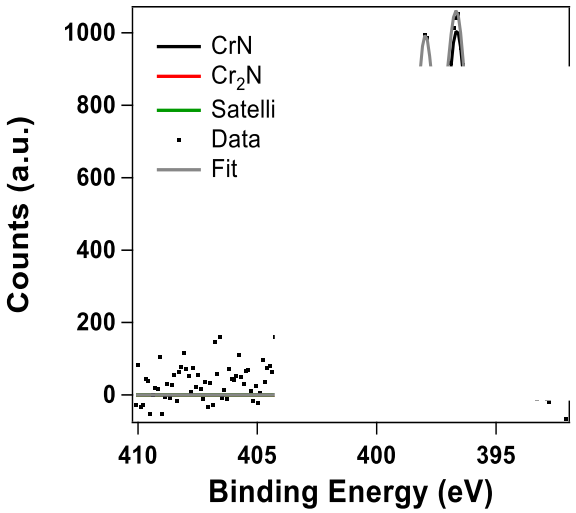
CrN

Cr_2N, CrO_xN_y

Satellite

N 1s region:
CrN - 396.5 eV
Cr_2N, CrO_xN_y - 397.8 eV
Satellite ~ 399 eV

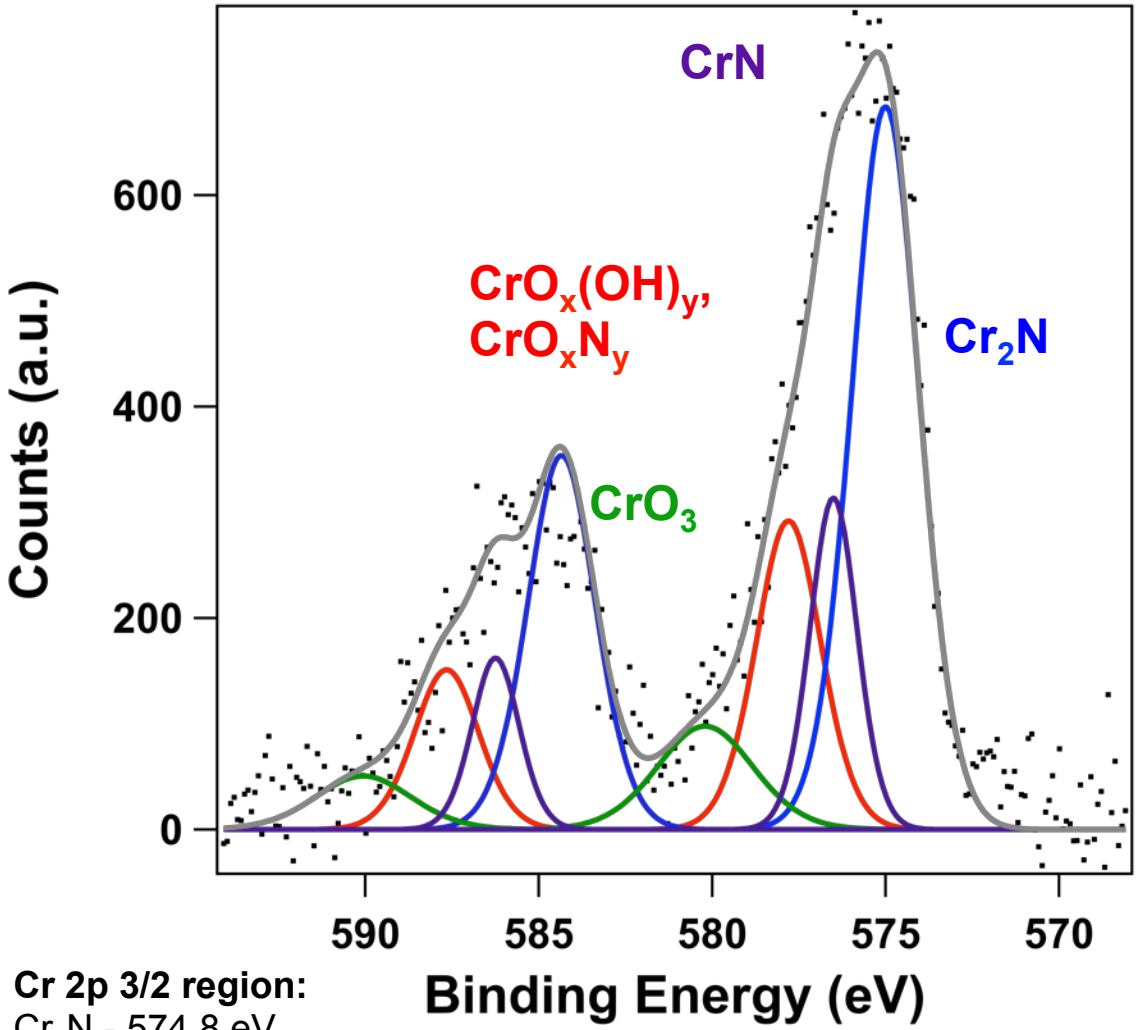
XPS Peak Assignments of Cr_2N



Cr_2N, CrO_xN_y

CrN

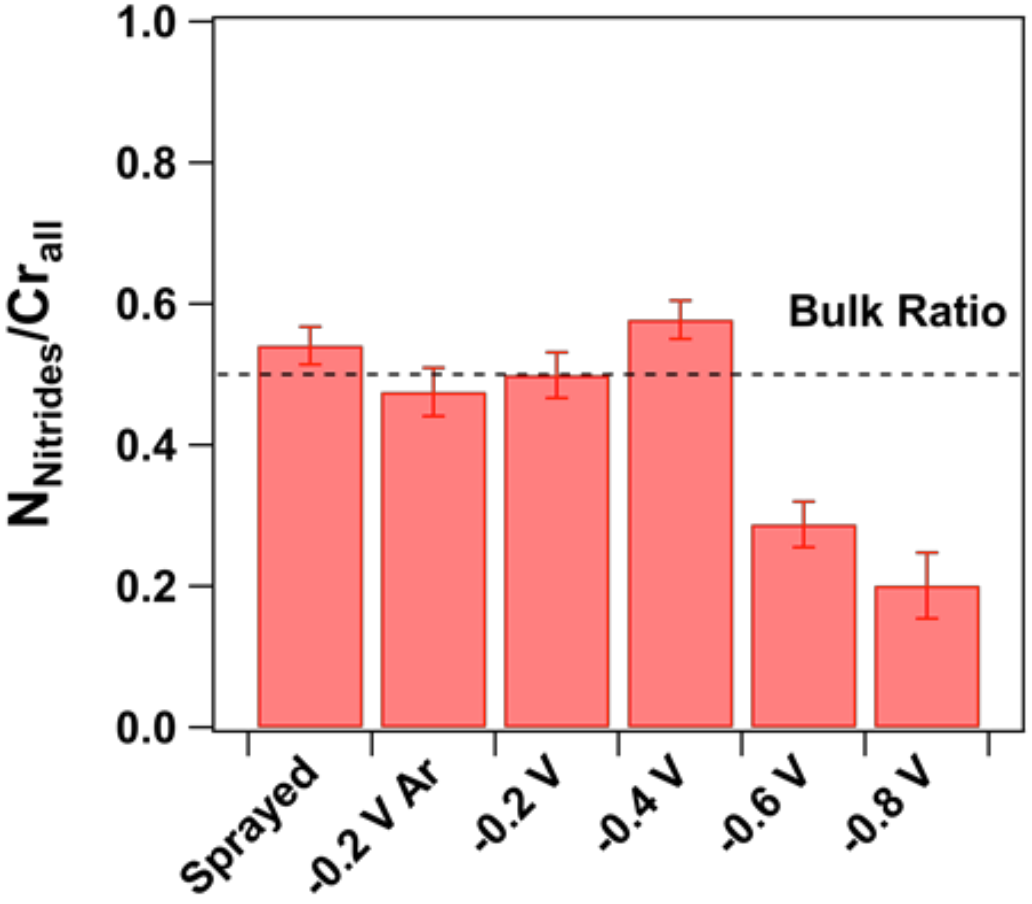
Satellite

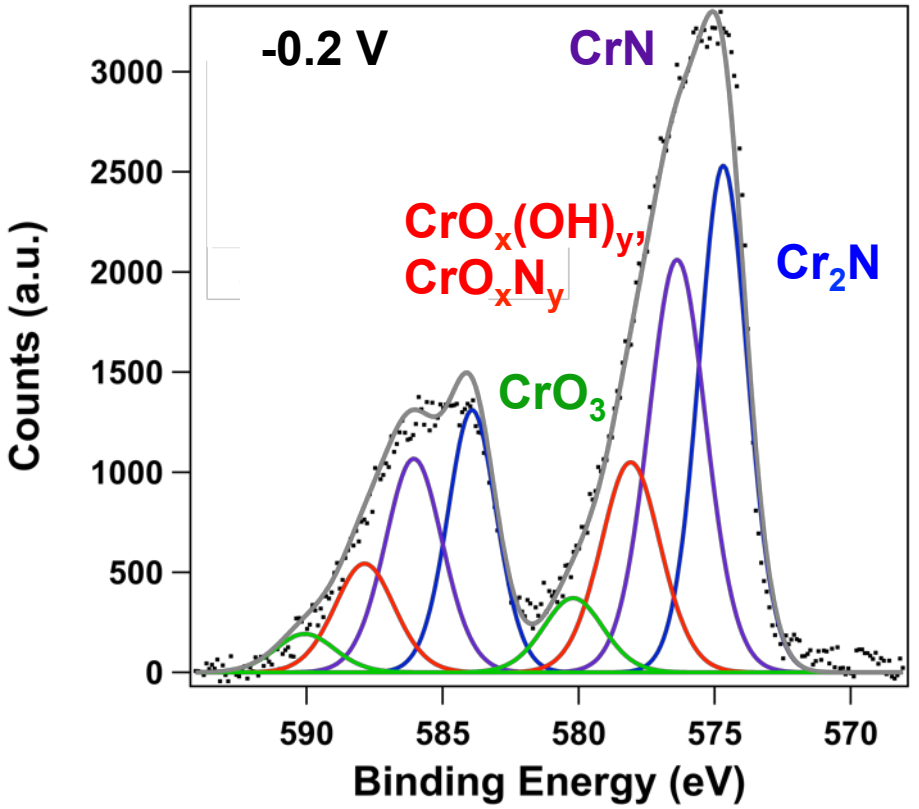


N 1s region:
CrN - 396.5 eV
Cr_2N, CrO_xN_y - 397.8 eV
Satellite ~ 399 eV

Cr 2p 3/2 region:
Cr_2N - 574.8 eV
CrN - 576.0 eV
$CrO_x(OH)_y$ - 577.4 eV
CrO_3 - 580.0 eV

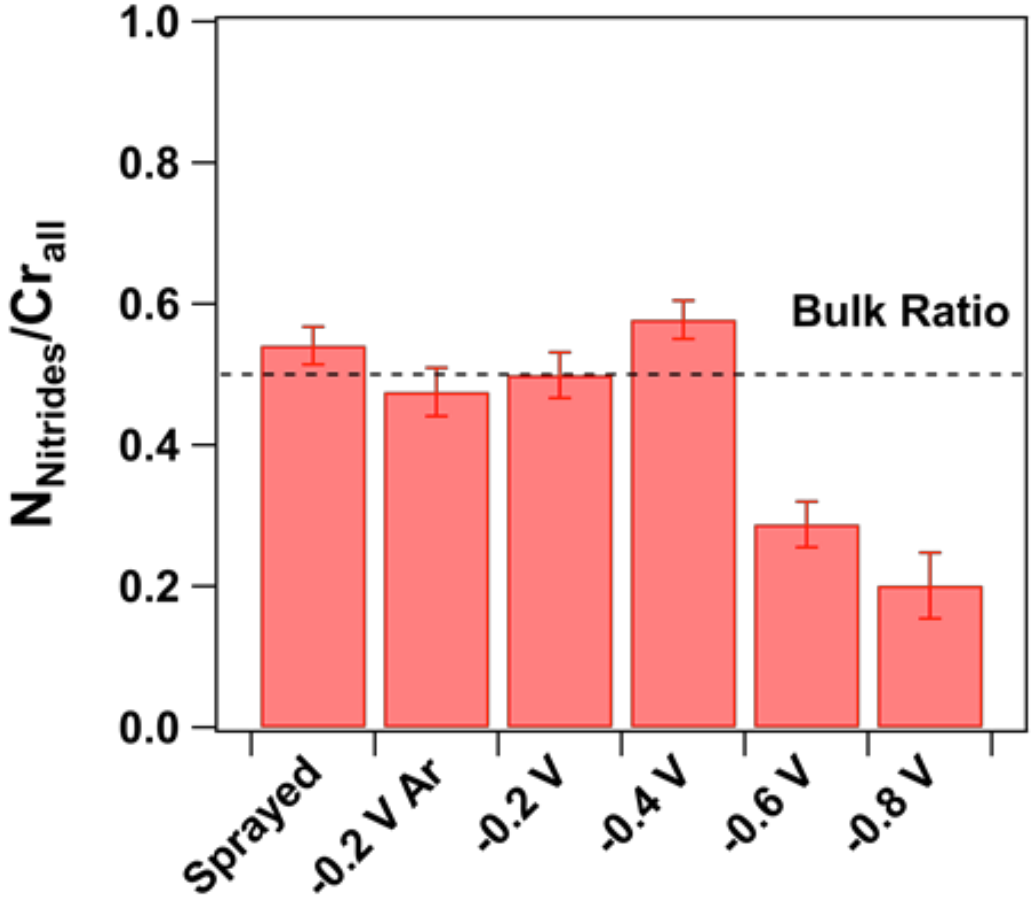
XPS Shows Nitride Loss Only for Lower Potentials

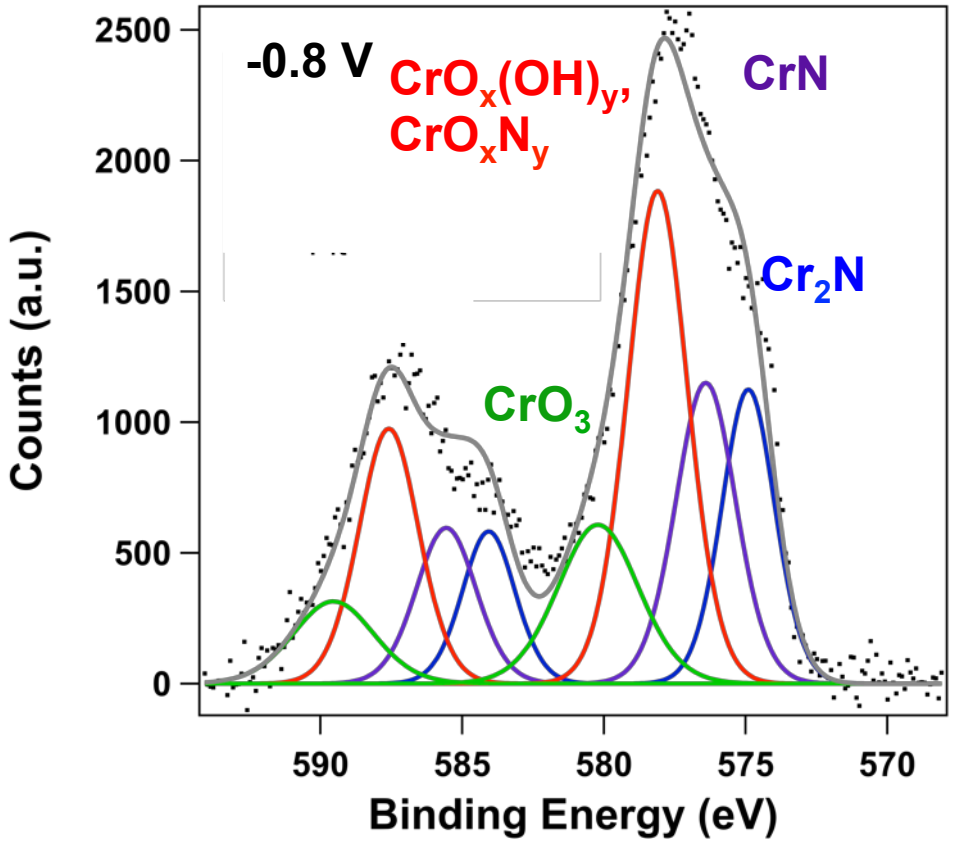




- Ratio of N:Cr shows loss of N at -0.6 and -0.8 V
  - Indicates nitride degrades at higher potentials

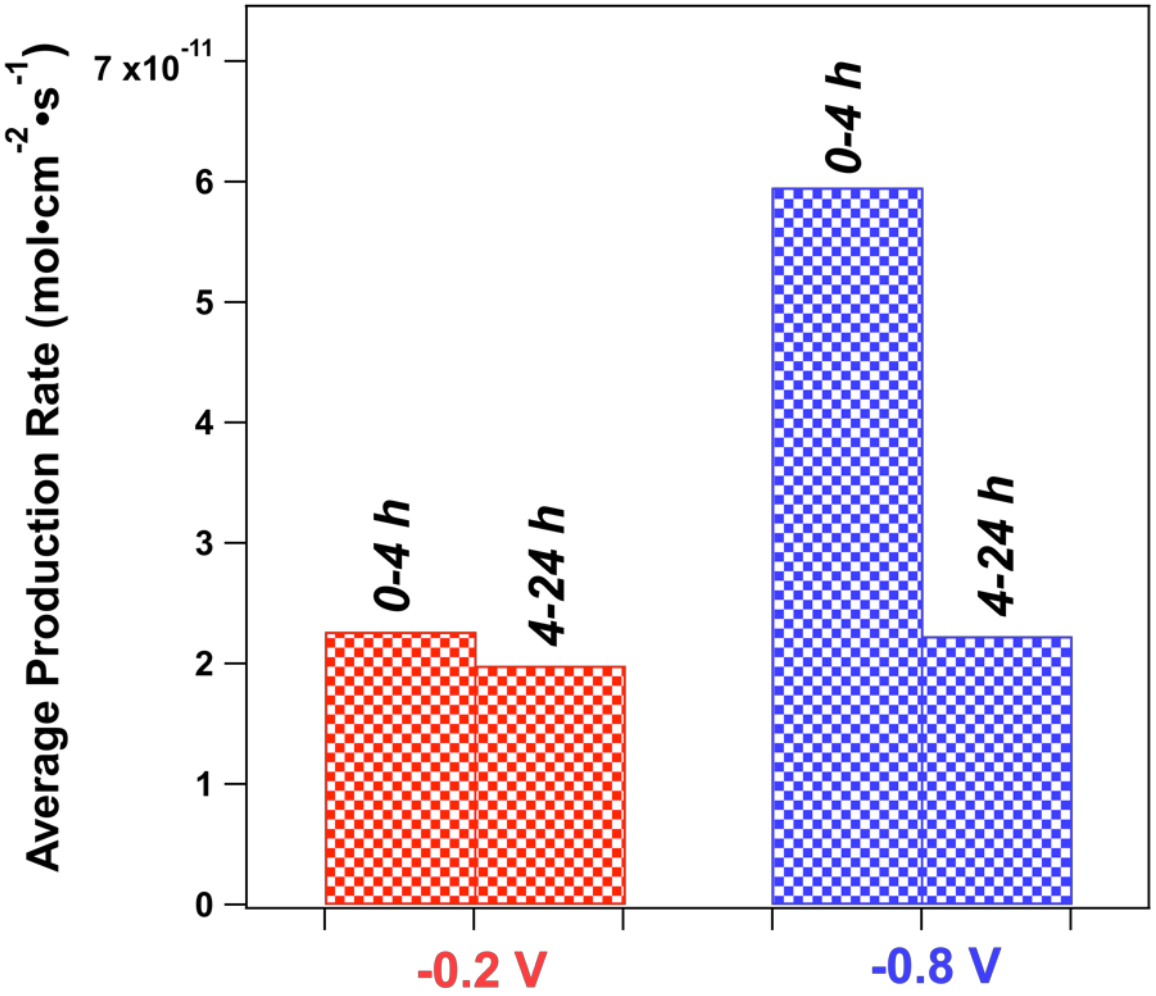
XPS Shows Nitride Loss Only for Lower Potentials





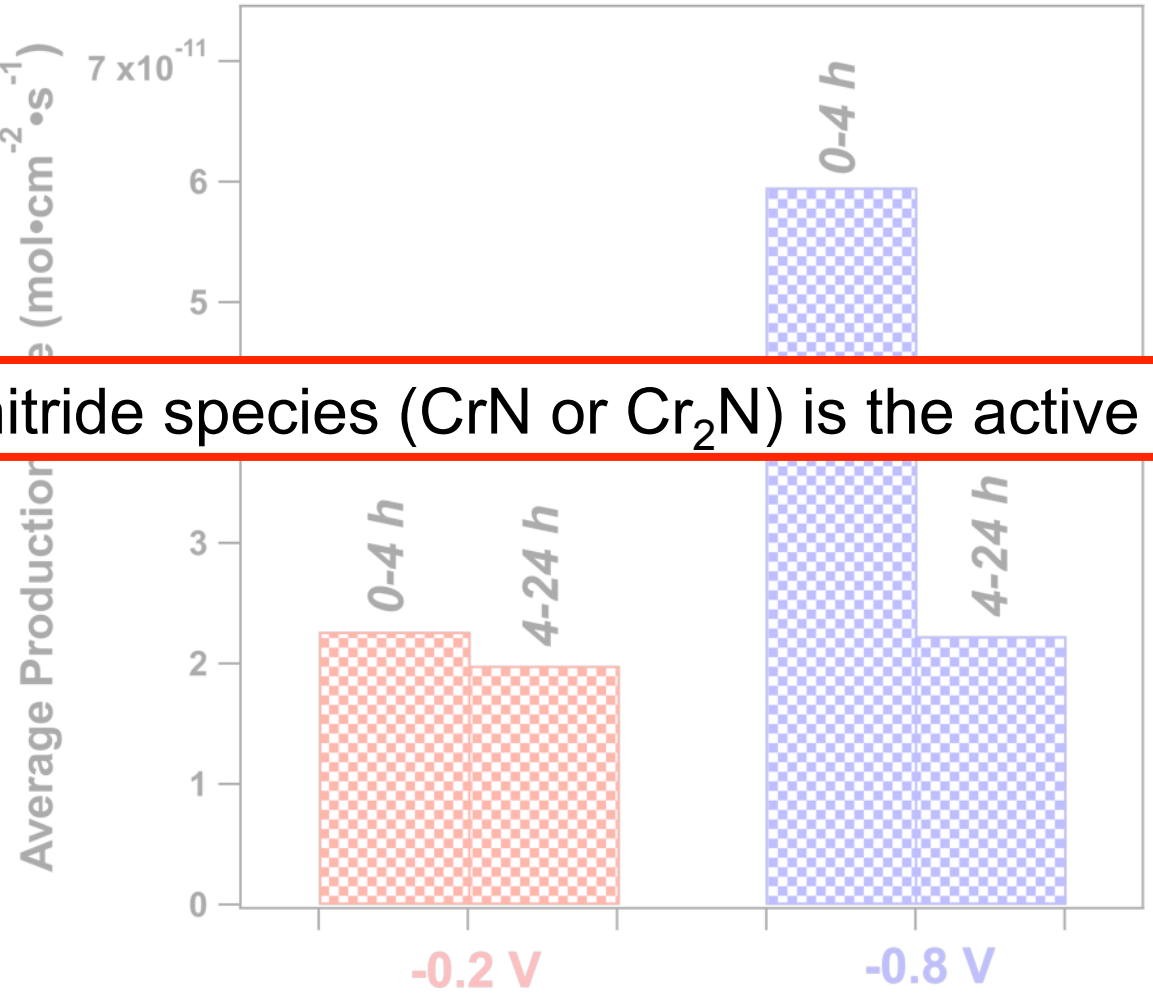
- Ratio of N:Cr shows loss of N at -0.6 and -0.8 V
  - Indicates nitride degrades at higher potentials

Lower Potentials Causes Significant Deactivation



Faster Deactivation at low potentials!
Nitride is the active species!

Lower Potentials Causes Significant Deactivation

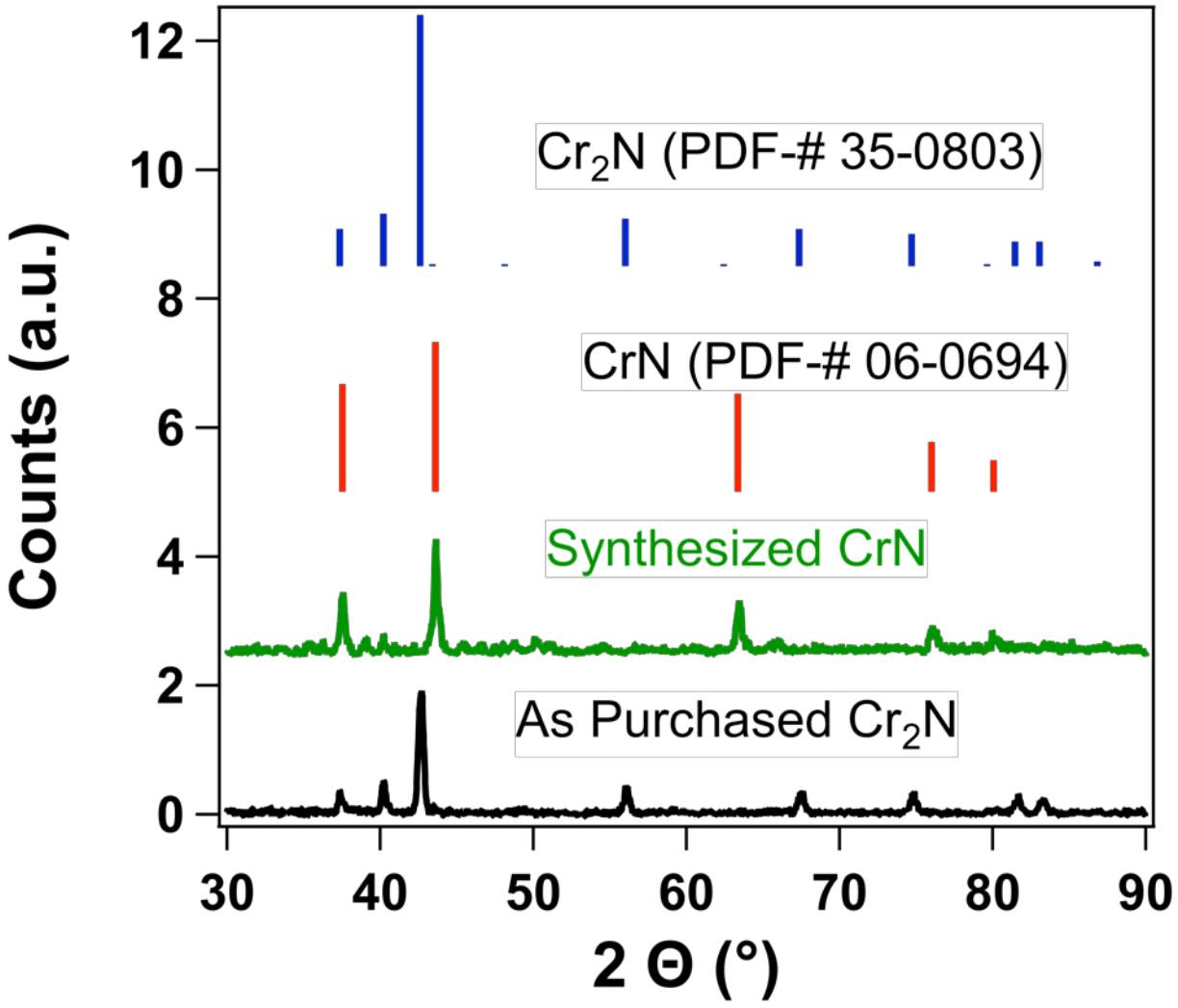


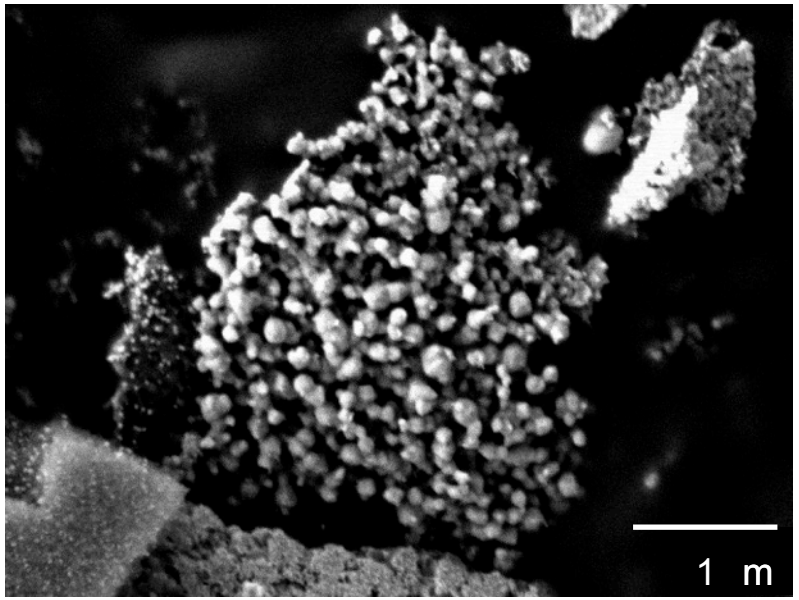
Which nitride species (CrN or Cr_2N) is the active species?

Faster Deactivation at low potentials!
Nitride is the active species!

Synthesized Nanoparticle CrN Catalyst

Synthesized using urea glass method[1]

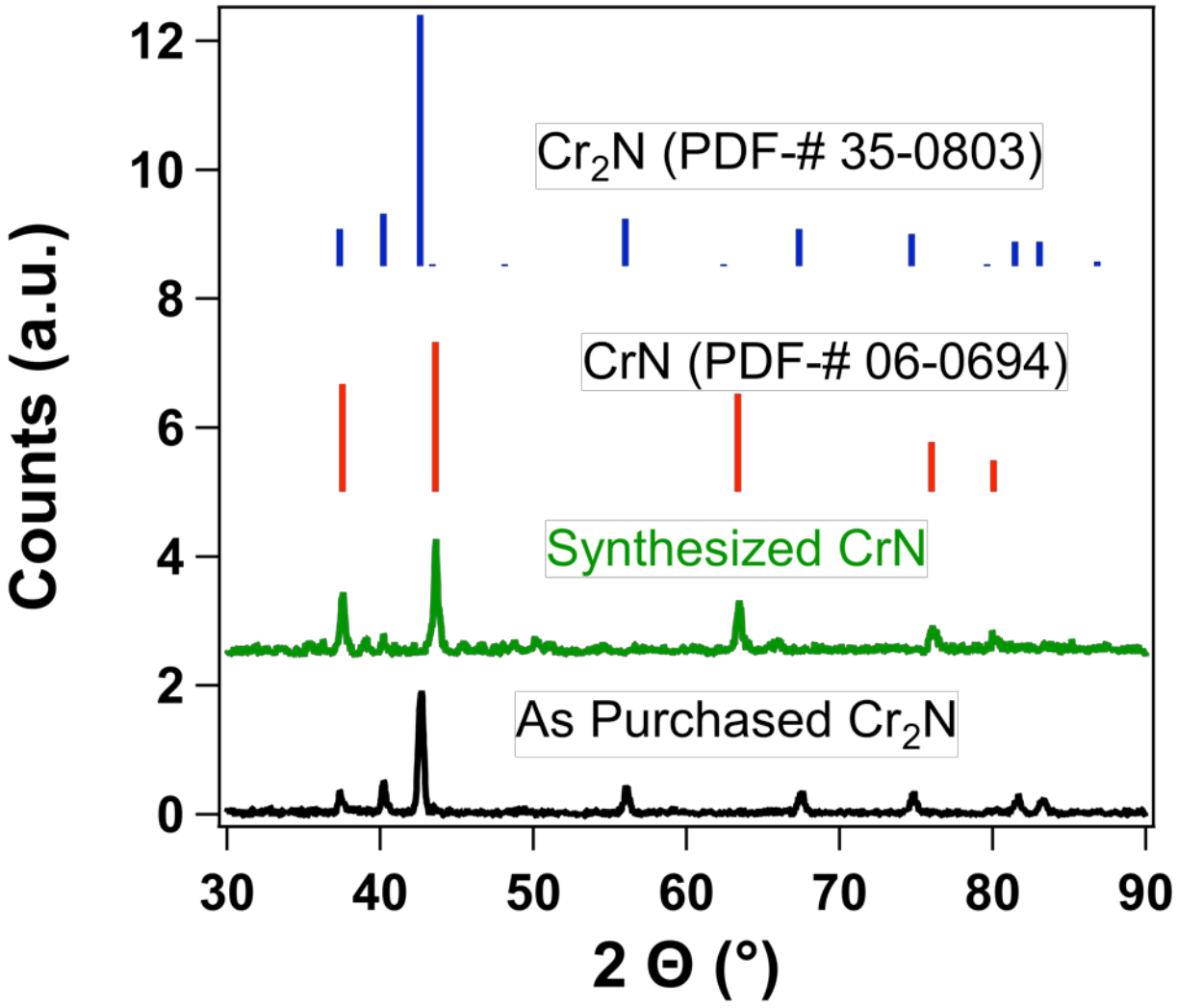


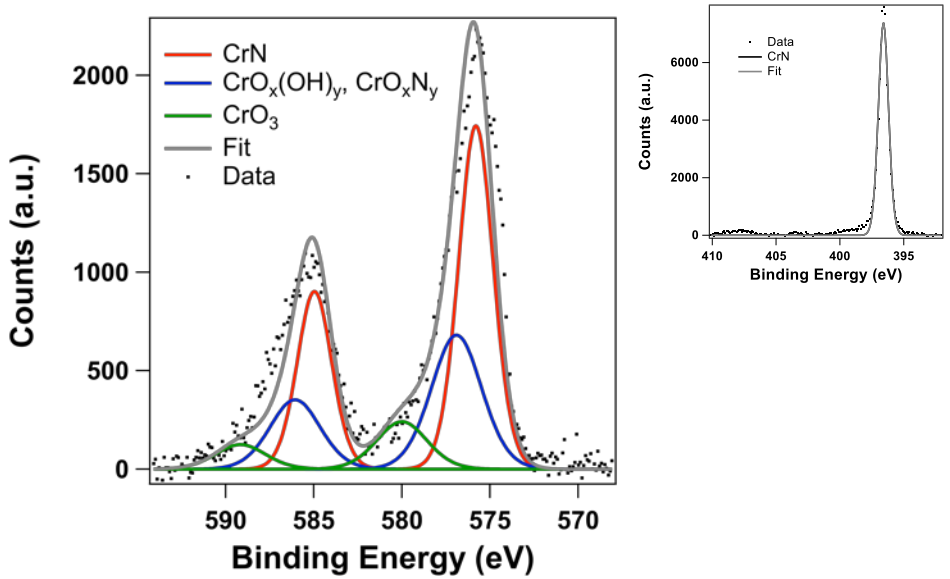


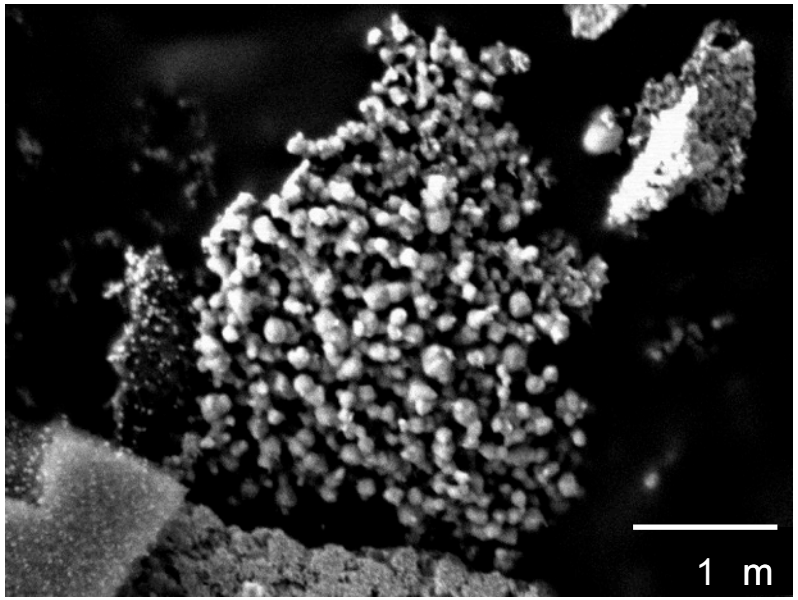
[1] *Chem. Mater.* 2009, 21, 21, 5136-5144

Synthesized Nanoparticle CrN Catalyst

Synthesized using urea glass method[1]

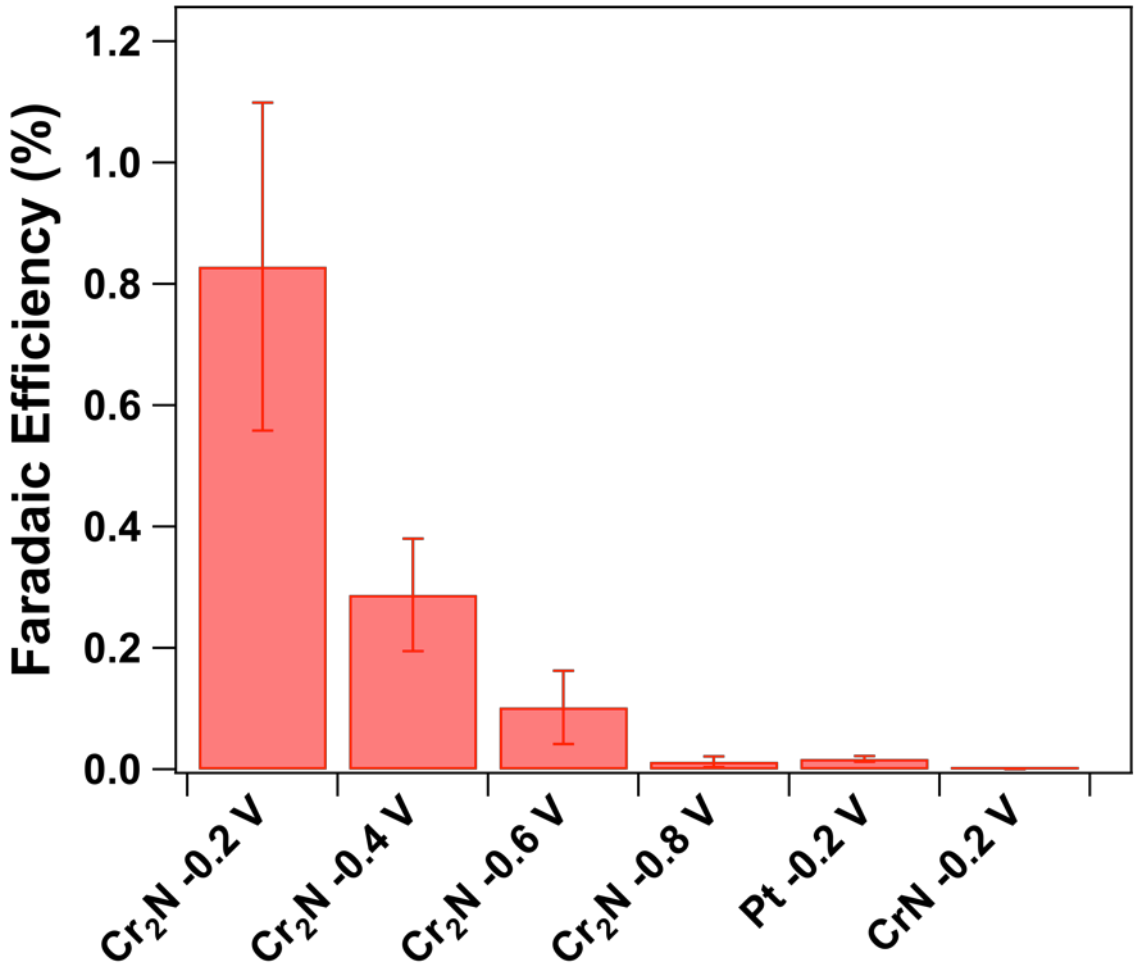


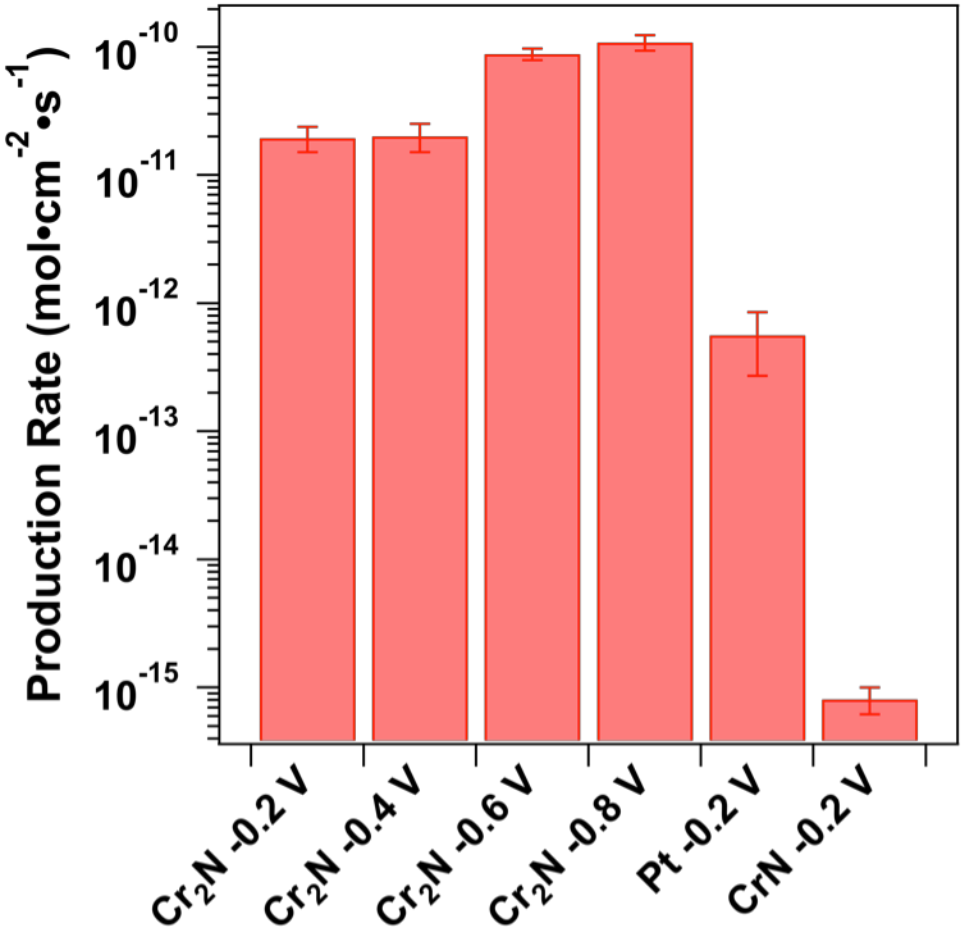




[1] *Chem. Mater.* 2009, 21, 21, 5136-5144

CrN is Not Active Compared to Cr_2N



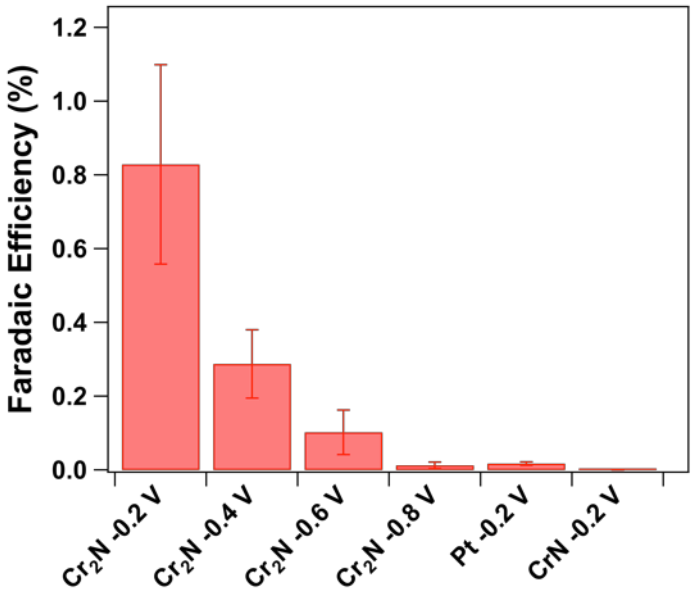


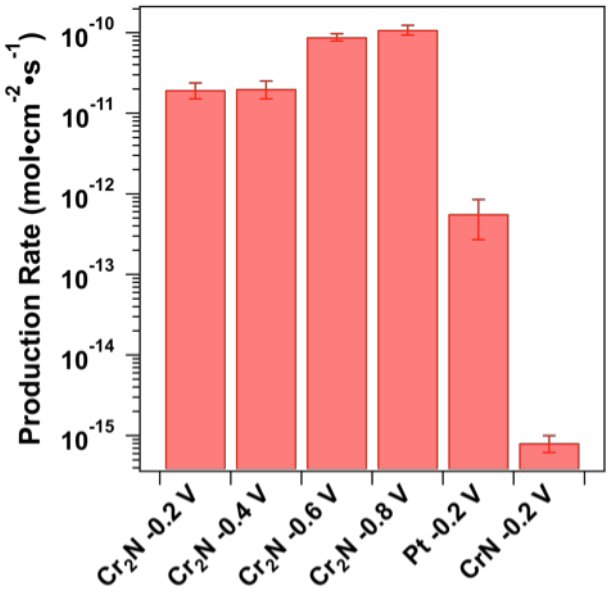
MEA Conditions:
0.4 mg/cm^2 Pt anode
1 mg/cm^2 Nitride cathode
0.1 L/min H_2 anode, N_2 cathode
80/85/85 ^{o}C cell, anode, cathode

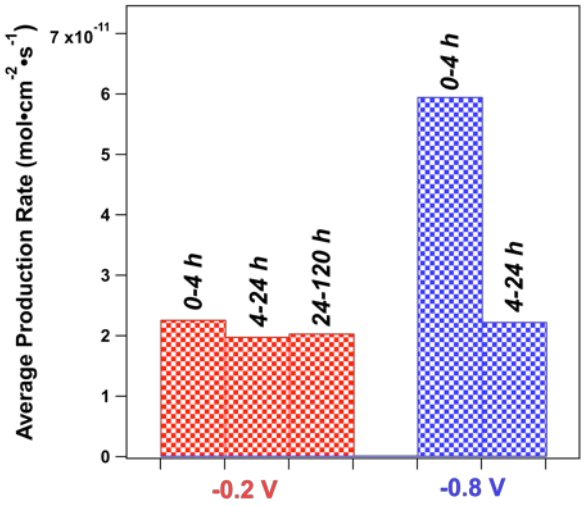
- CrN has low FE and low Production Rates compared to Cr_2N and Pt
- **Cr_2N is the active species**

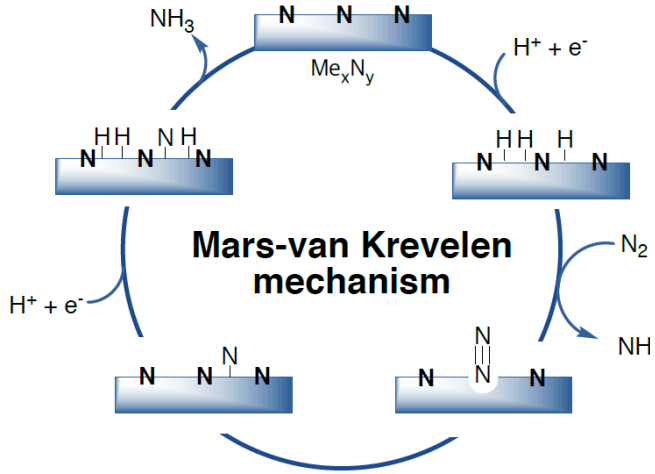
Conclusions

- Nitrides show 50 fold increase in FE and specific production rates over Pt
  - Increasing overpotential favors HER
- Low overpotential is activating N_2 gas to produce NH_3
  - No change in the composition of the surface
- Higher overpotentials show loss of nitrogen and significant catalyst deactivation
  - Nitride is the active component for ammonia production
- Consistent with a Mars-van Krevelen type mechanism





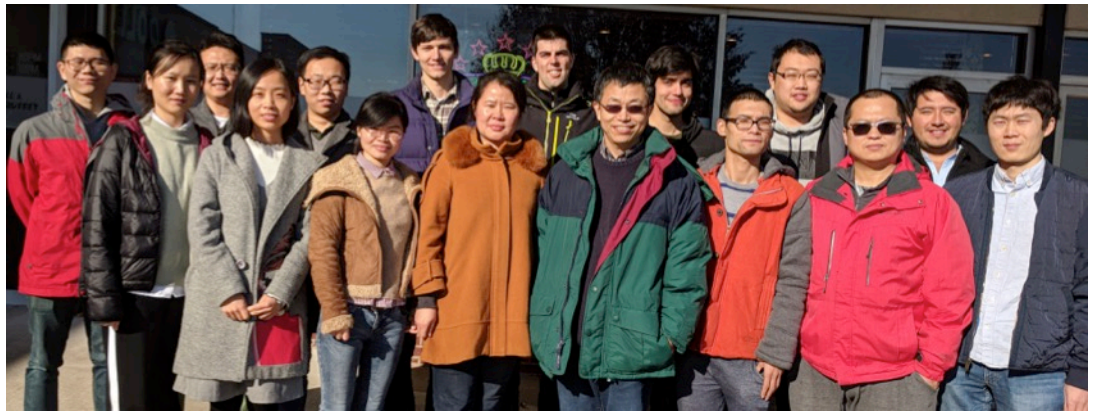




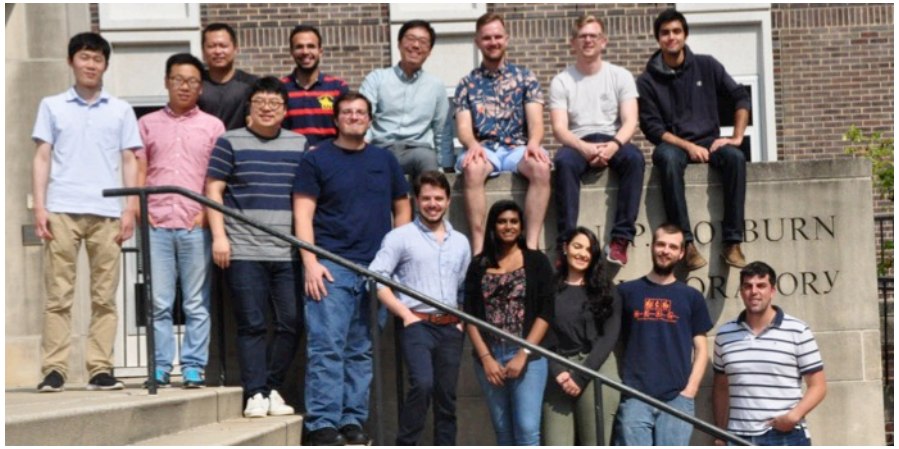
Acknowledgements

- Dr. Bingjun Xu
- Dr. Yushan Yan
- Xuan Yang
- Jacob Anibal
- Xu and Yan groups
- University of Delaware
- DOE EPSCoR (DE-SC0016537)

Yan Group



Xu Group



Cr_2N Turnover Frequency Calculation

Production Rate of N/s

$$1 * 10\uparrow -6\ mol\ N/day * 1\ day/86400\ s * 6.02 * 10\uparrow 23\ atoms/1\ mol = 6.97 * 10\uparrow 12\ \ atoms\ N/s$$

Total Surface Atoms of Cr_2N

$$5\ mg\ Cr\downarrow 2\ N * 13.2 cm\uparrow 2\ /mg * 1 * 10\uparrow 15\ atoms/cm\uparrow 2\ = 6.6 * 10\uparrow 16\ \ surface\ atoms$$

Turnover Frequency of Cr_2N

$$TOF = Production\ Rate/Surface\ Atoms = 6.97 * 10\uparrow 12\ atomsN/s\ /6.6 * 10\uparrow 16\ \ atoms = 1 * 10\uparrow -4\ \ s\uparrow -1$$