Mechanistic Insights into Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride Nanoparticles

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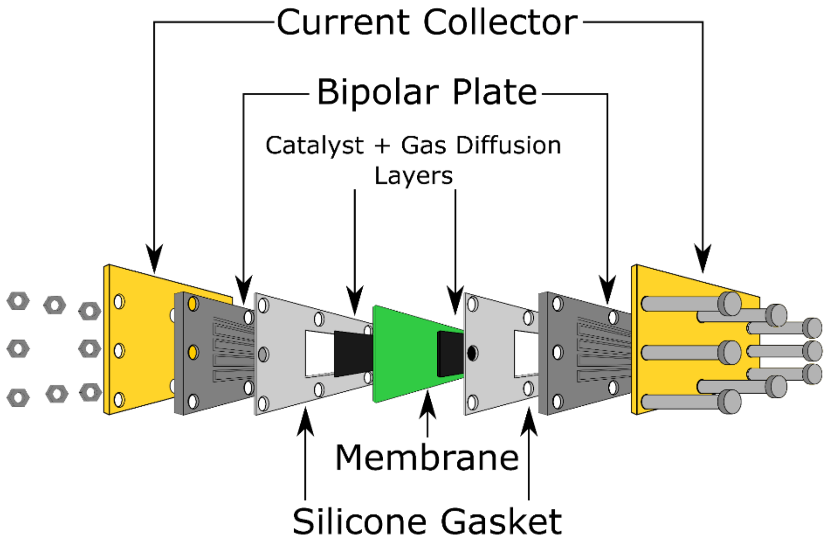
Setup and Quantification of Ammonia



Cathode: 0.5 mg cm^{-2} VN (N_2)

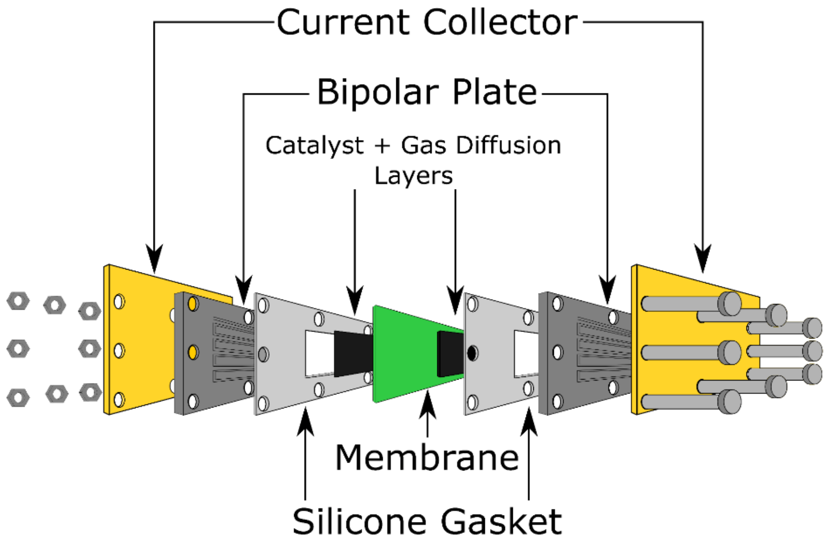
Anode: 0.4 mg cm^{-2} Pt (H_2)

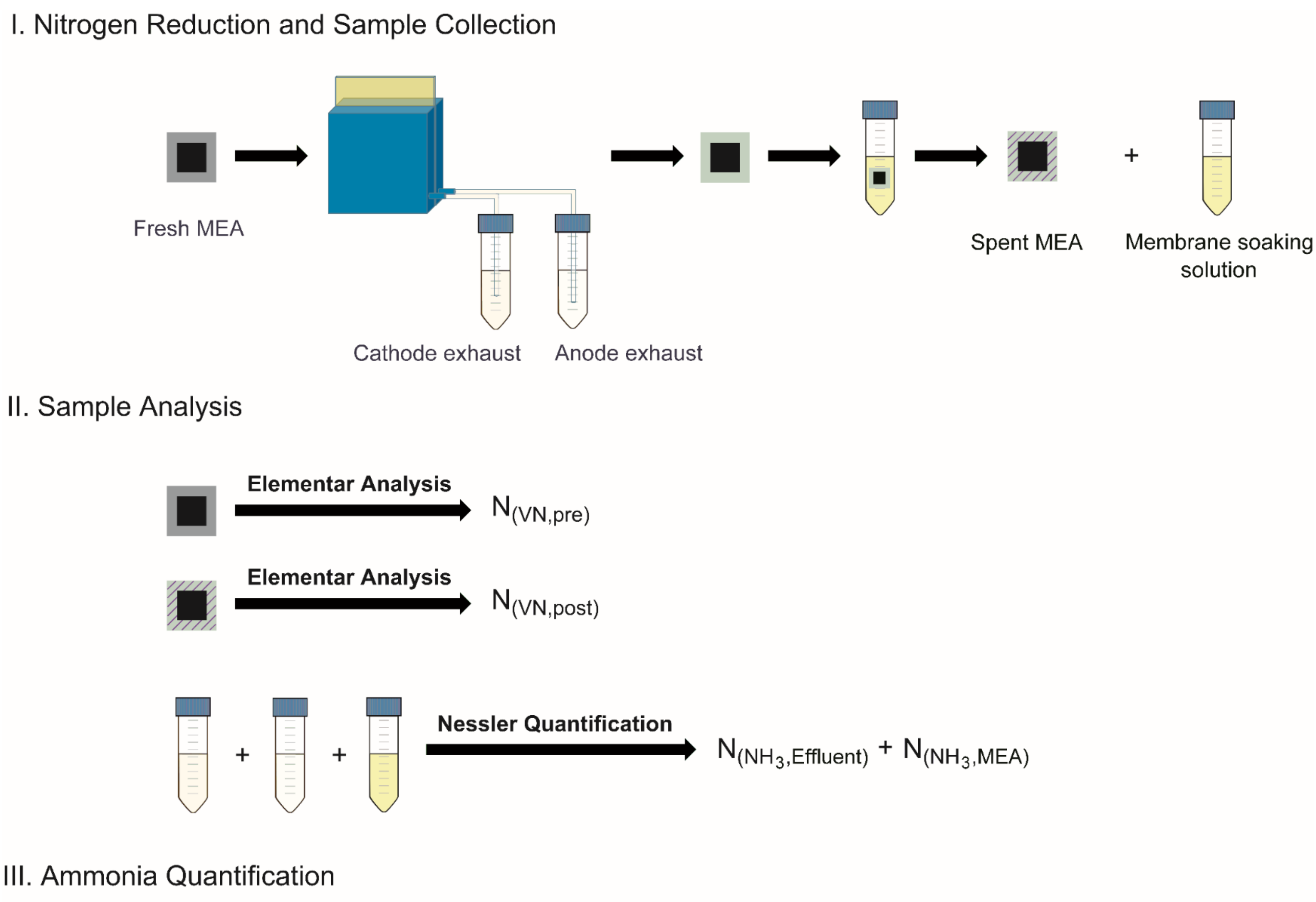
Electrolyte: Nafion-211 membrane

- **Membrane electrode assembly (MEA) configurations provide reliable activity measurements**

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

Setup and Quantification of Ammonia



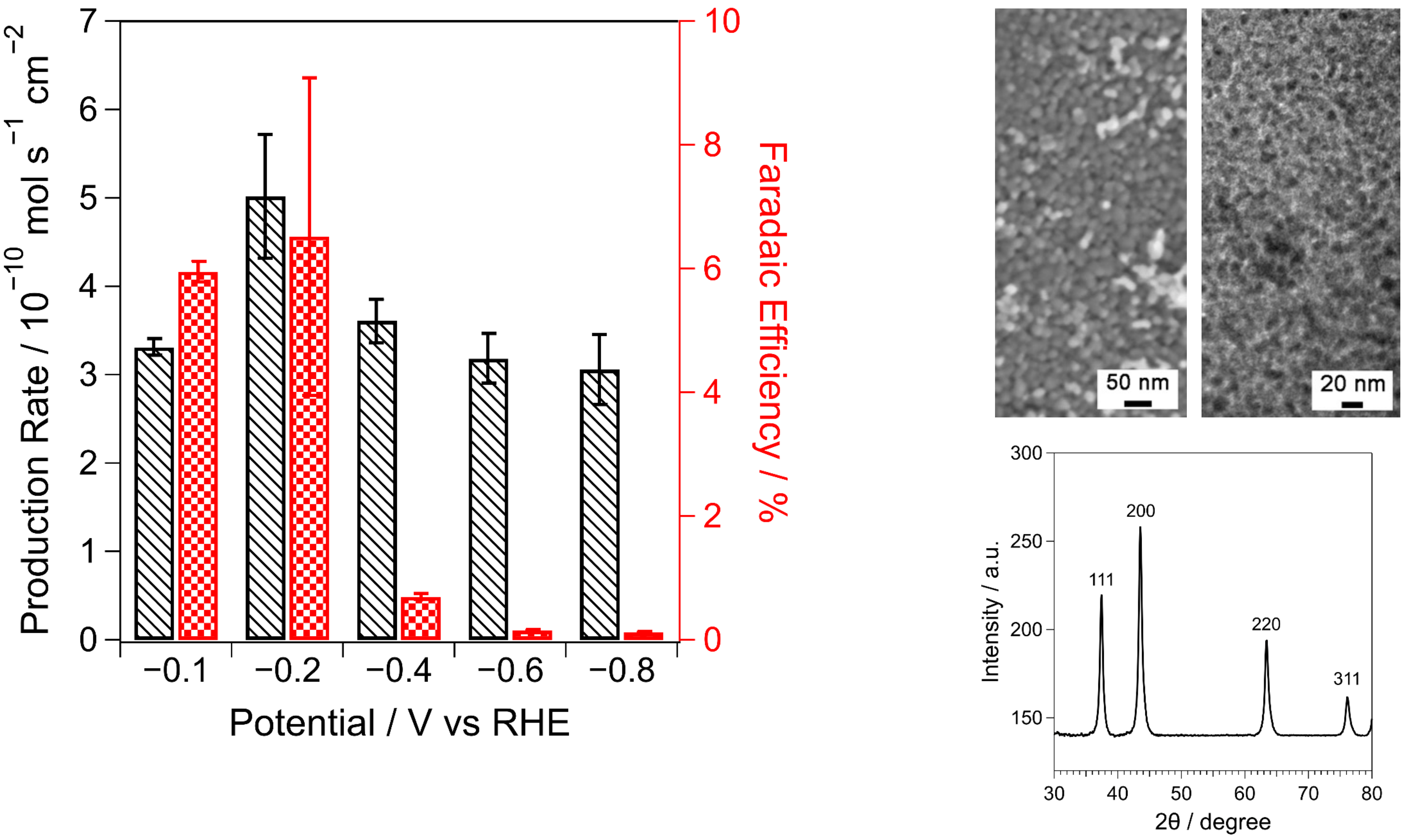


$$N_{(NH_3,ENRR)} = N_{(NH_3,Effluent)} + N_{(NH_3,MEA)} + N_{(VN,post)} - N_{(VN,pre)}$$

- **Membrane electrode assembly (MEA) configurations provide reliable activity measurements**
- **N mass balance enables the reliably quantification of produced ammonia**

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

VN is an Active, Selective and Stable ENRR Catalyst



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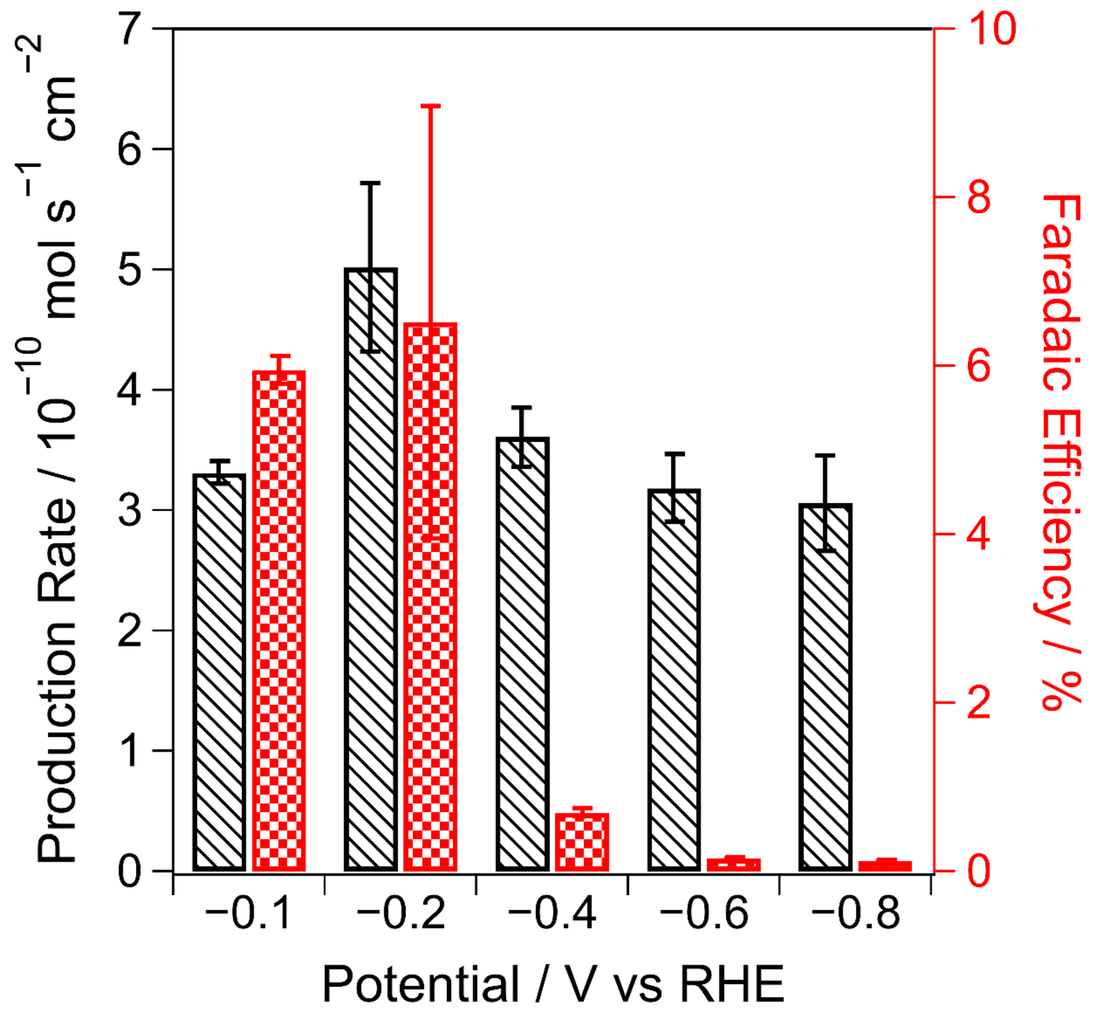

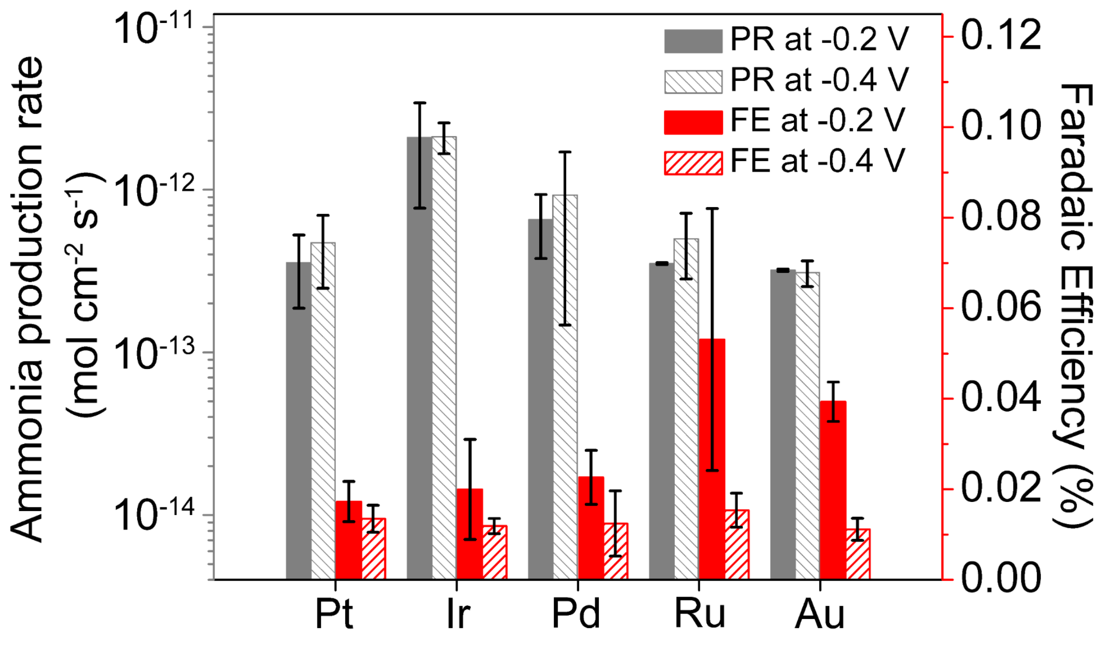

VN is more than two orders of magnitude more active and selective than noble metal catalysts

Nash et al. *J. Electrochem. Soc.* **2017**, *164*, F1712−F1716

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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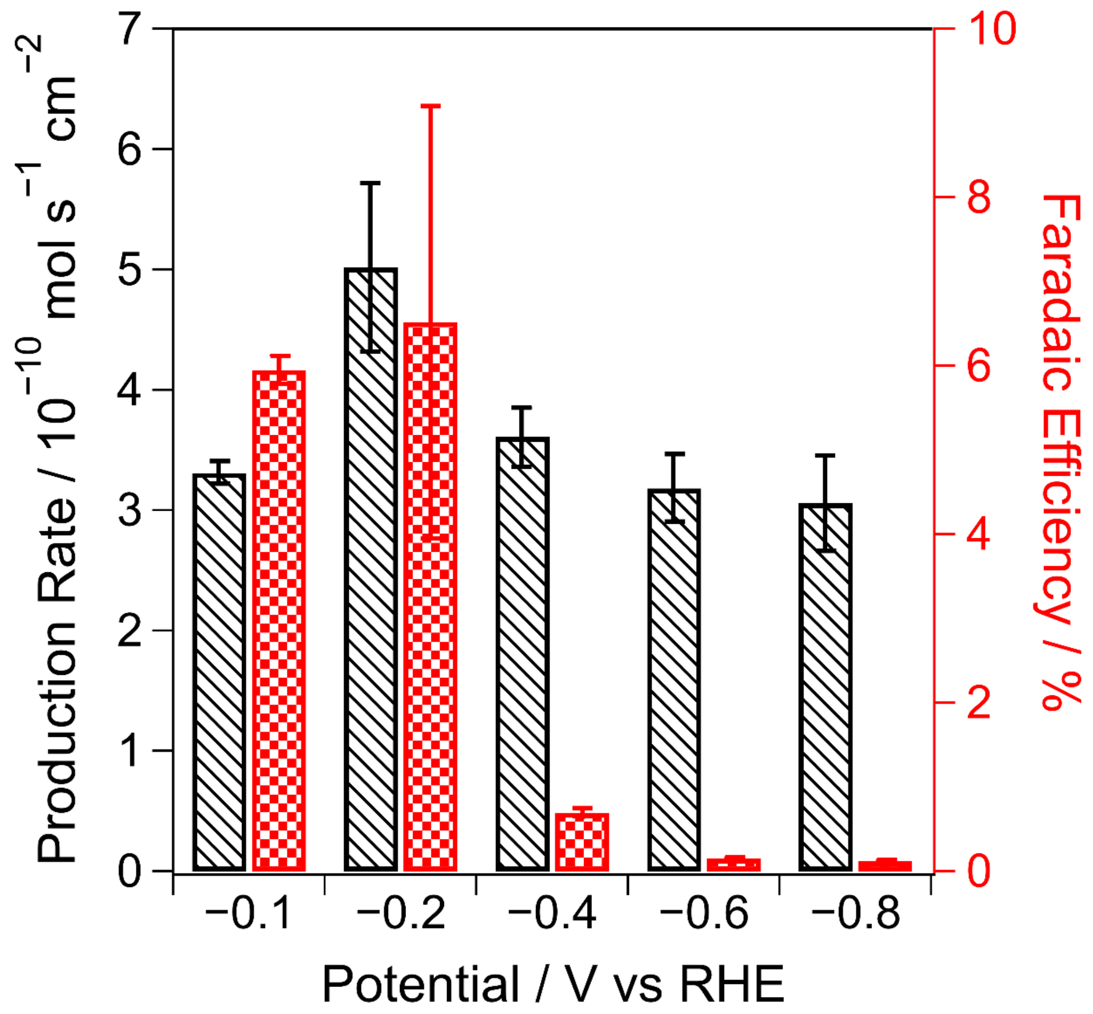
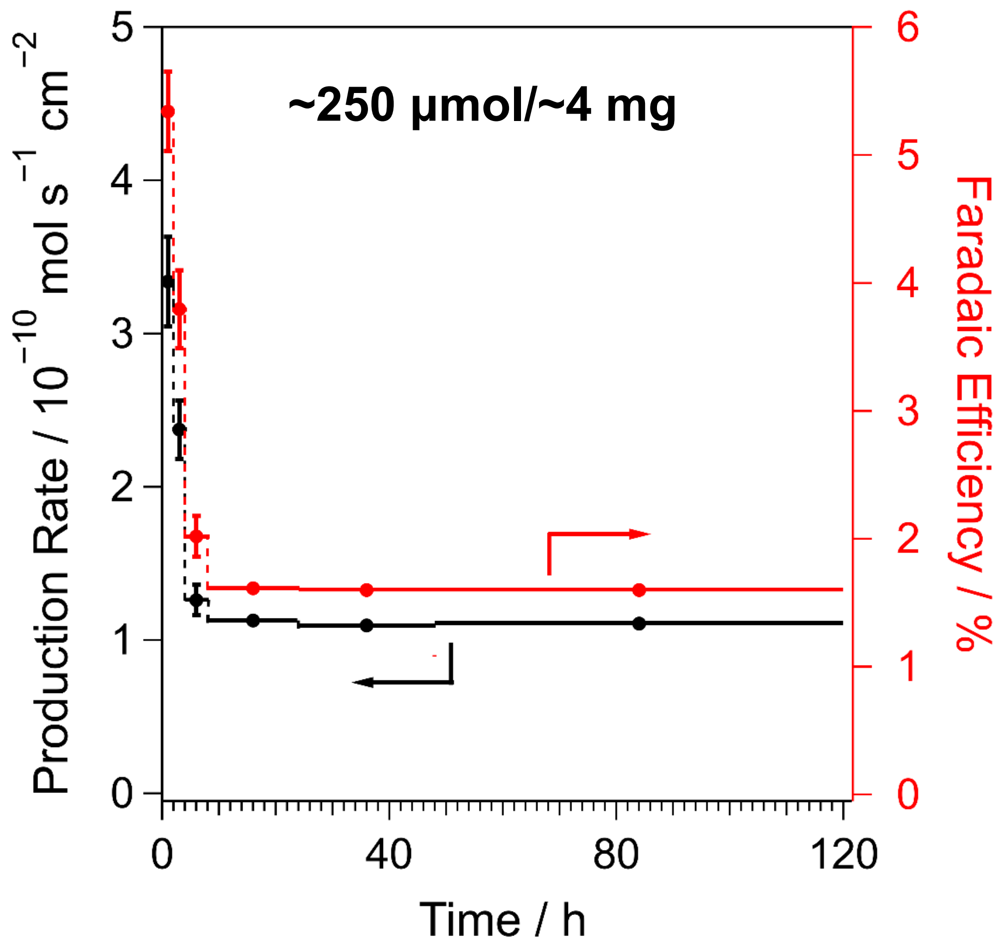
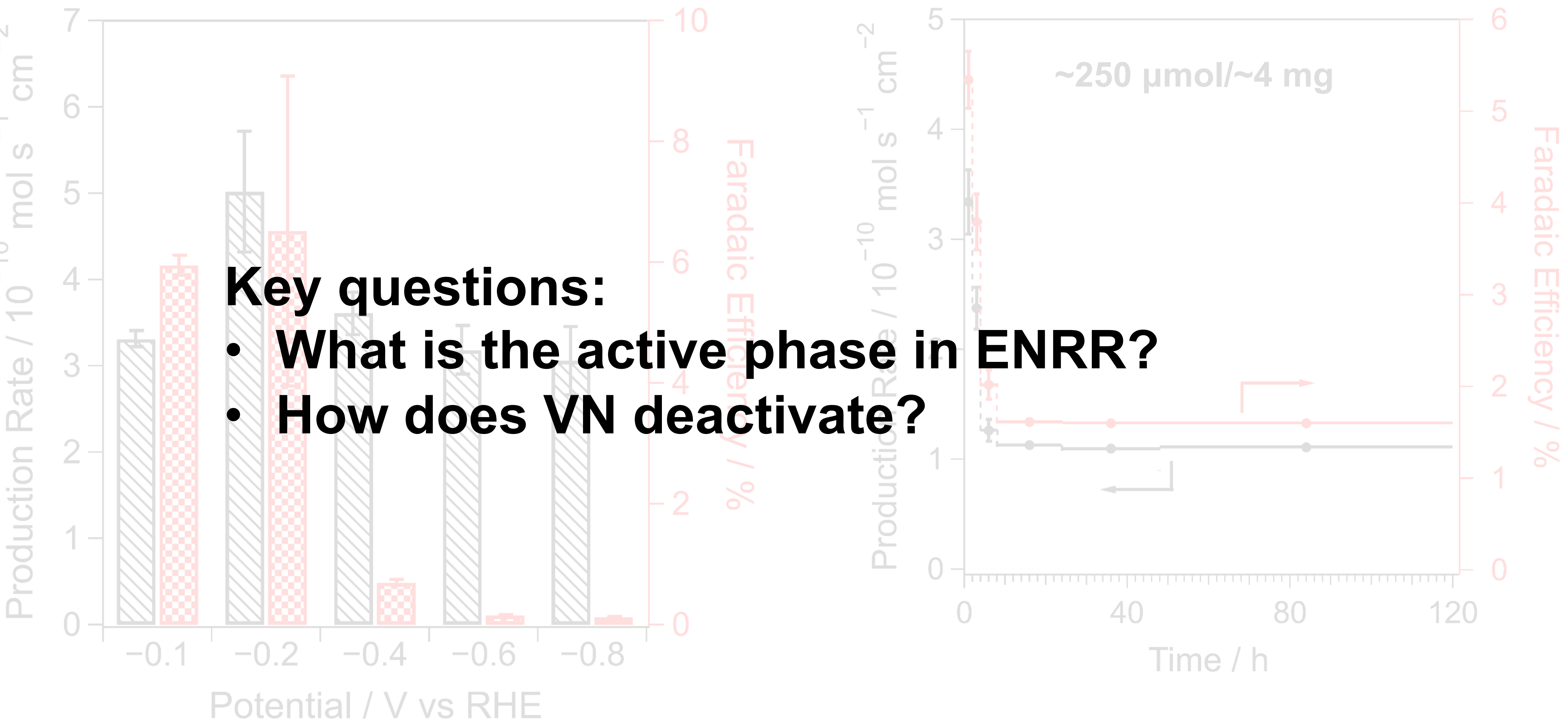




ENRR rate of 10^{-10} mol s^{-1} cm^{-2} can be maintained for 120 h

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

VN is an Active, Selective and Stable ENRR Catalyst



Key questions:

- **What is the active phase in ENRR?**
- **How does VN deactivate?**

ENRR rate of 10^{-10} mol s^{-1} cm^{-2} can be maintained for 120 h

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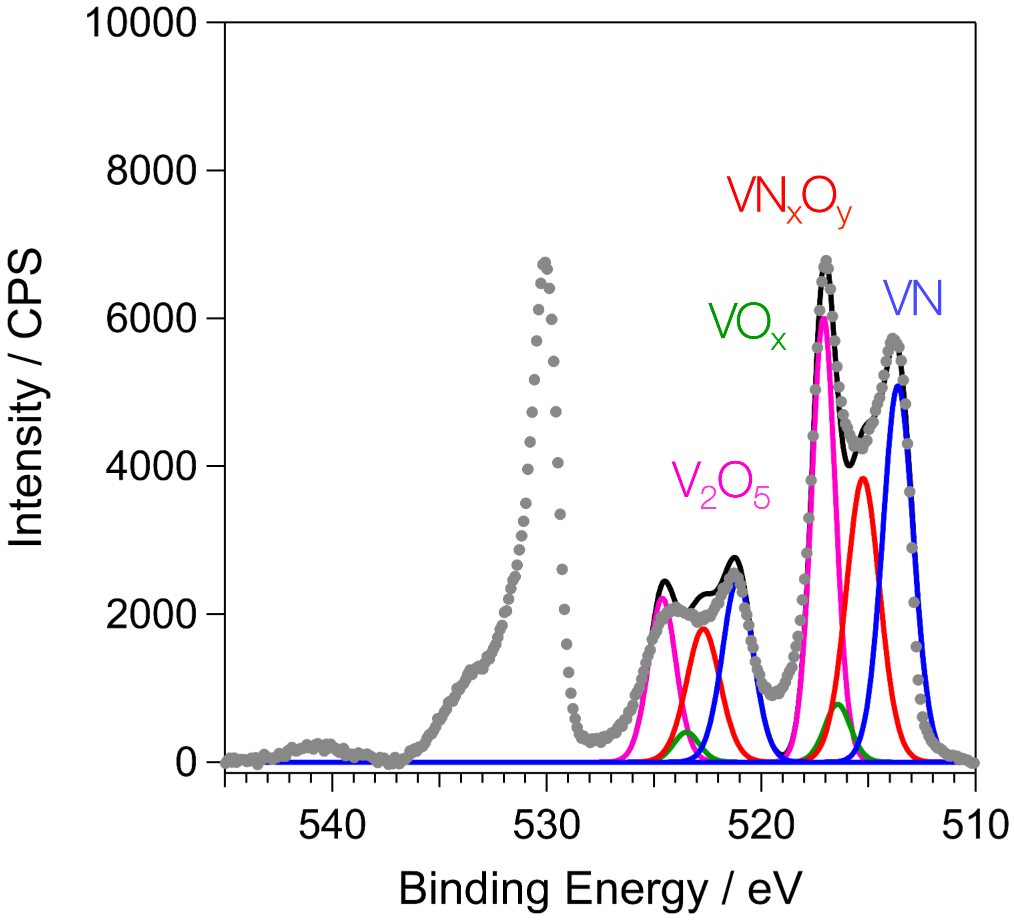
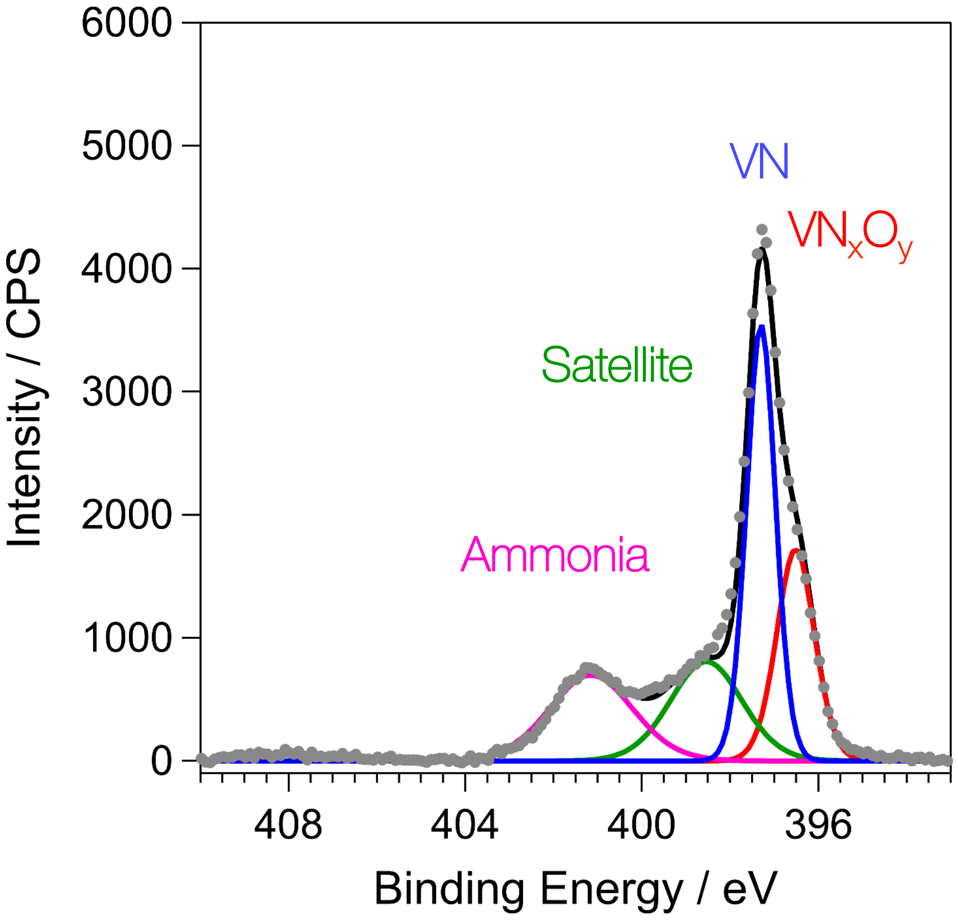
XPS of VN Catalysts before ENRR

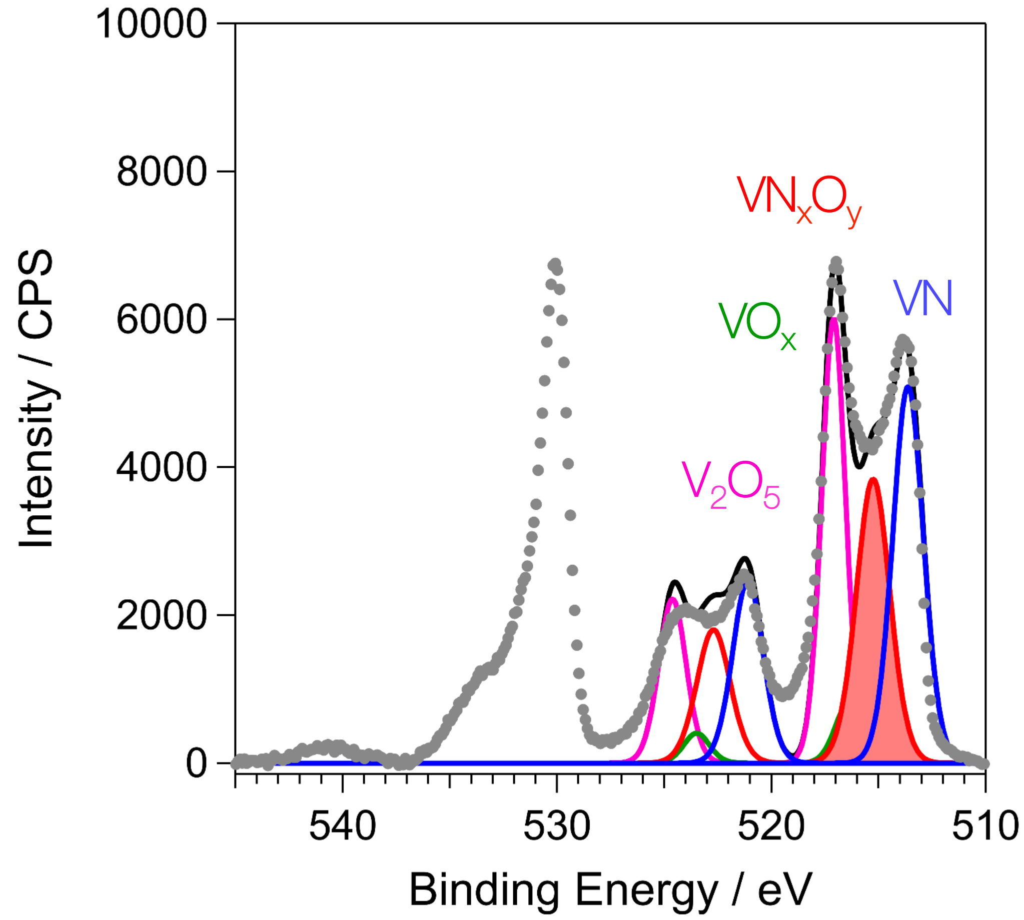


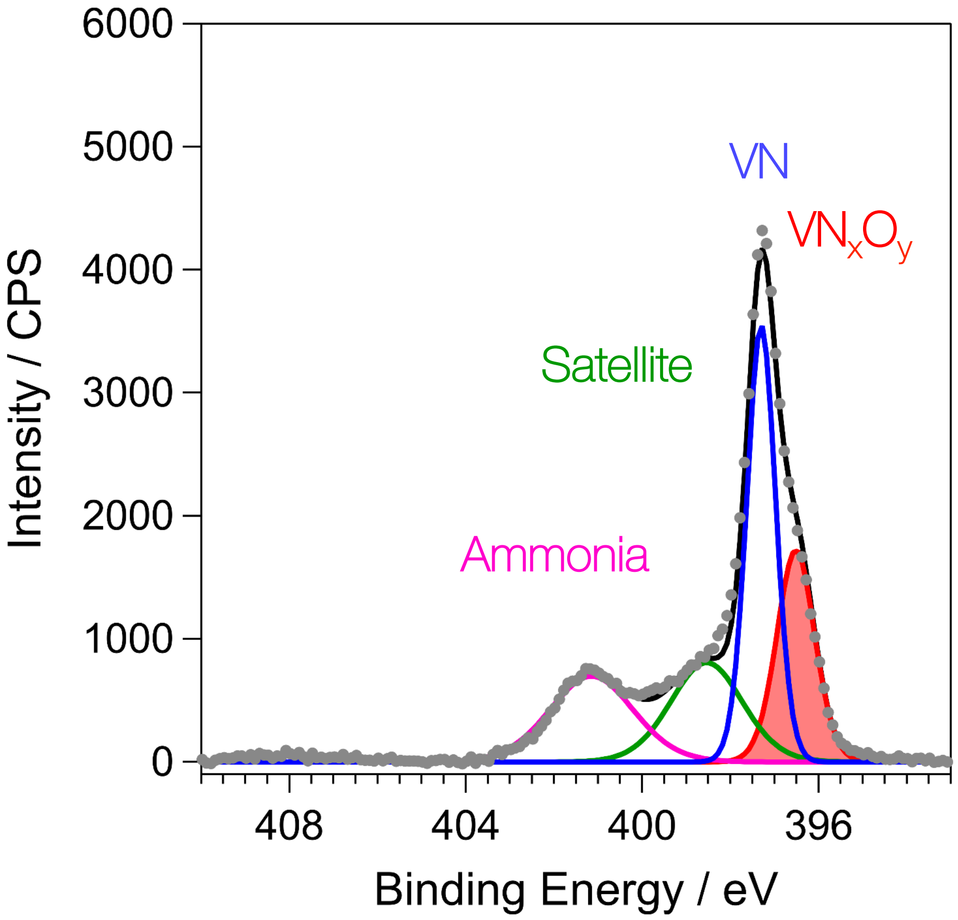


V 2p 3/2 region:
VN - 513.63 eV
VN_xO_y - 515.09 eV
VO_x - 515.99 eV
V_2O_5 - 517.10 eV

N 1s region:
VN - 397.3 eV
VN_xO_y - 396.4 eV
Satellite - 398.4 eV
Ammonia - 401.0 eV

XPS of VN Catalysts before ENRR





Based on the ratio of V 2p and N 1s bands assigned to VN_xO_y, and assuming a +3 oxidation state of V, the composition of the oxynitride is $VN_{0.7}O_{0.45}$

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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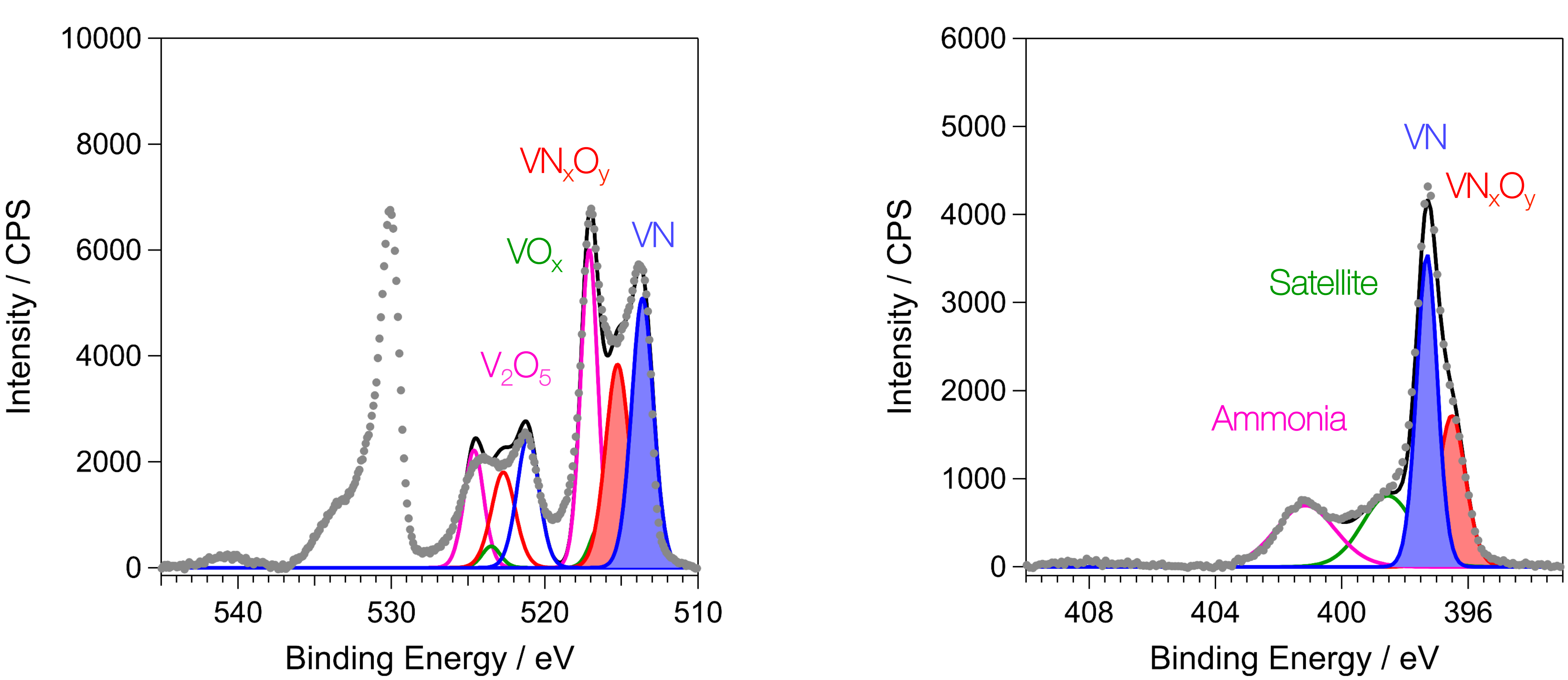

$VN_{0.7}O_{0.45}$: VN ratio on the fresh VN is ~0.91

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

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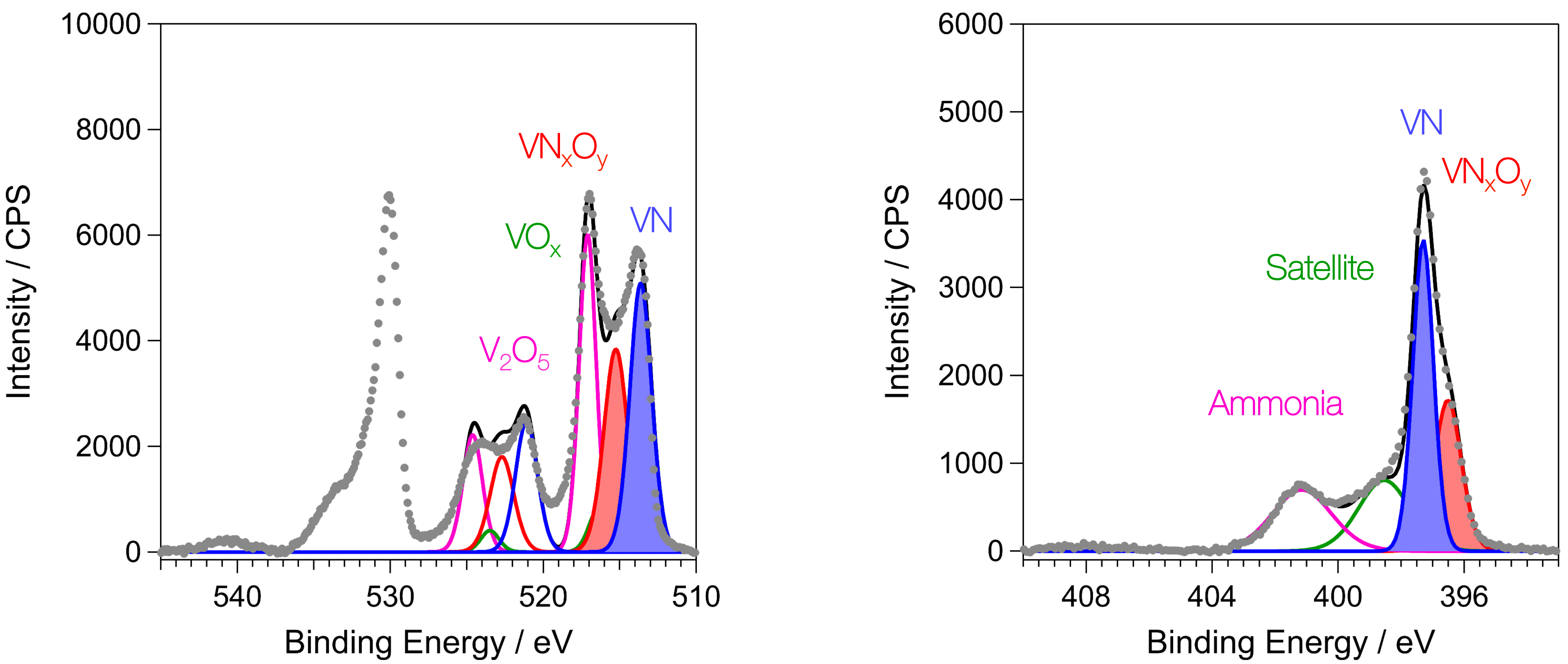
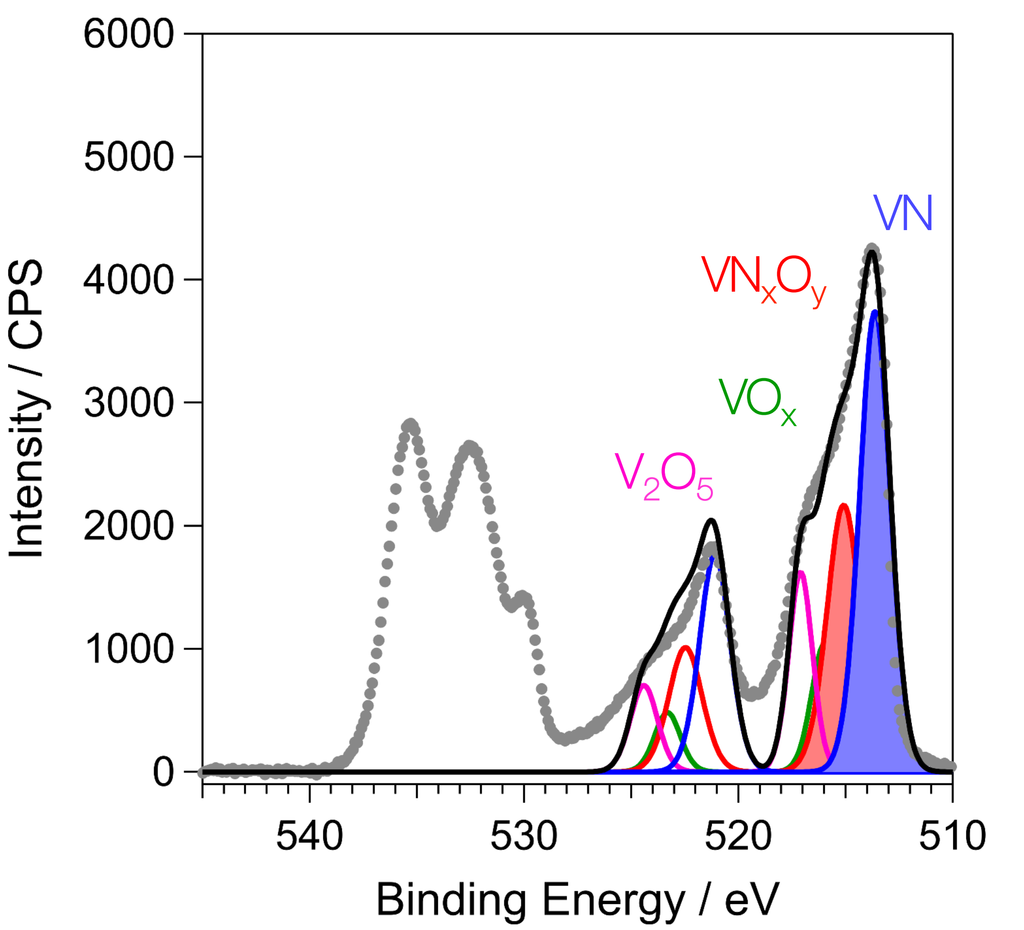
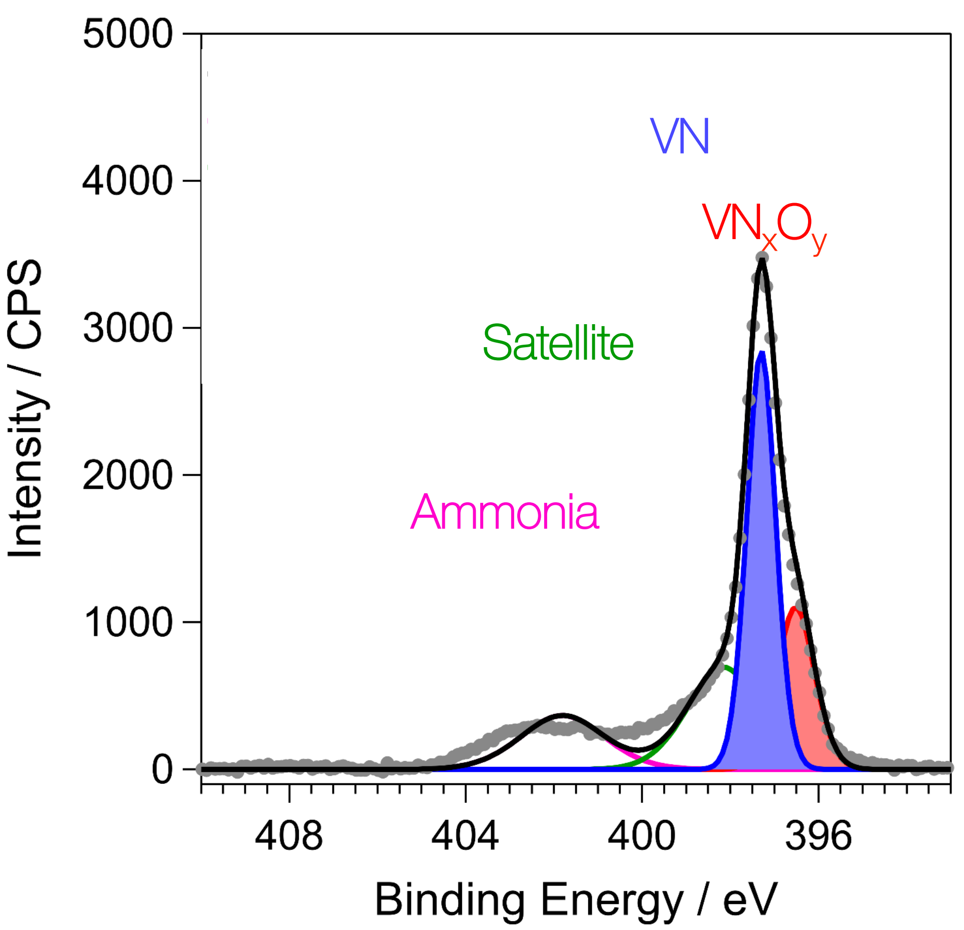


$VN_{0.7}O_{0.45}$: VN ratio on the fresh VN is ~0.91

How does the surface composition change during ENRR?

XPS of VN Catalysts after ENRR





$VN_{0.7}O_{0.45}$: VN ratio decreases to 0.77 after ENRR at −0.1 V for 1 h

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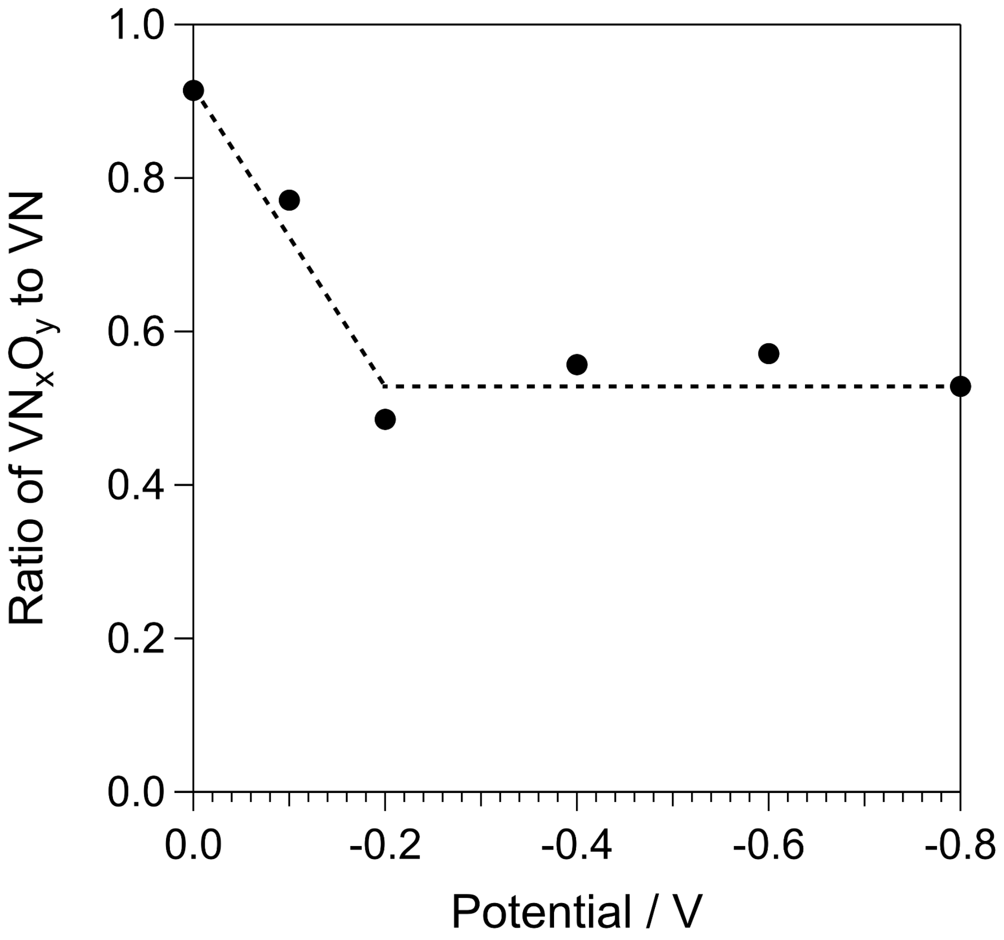
XPS of VN Catalysts after ENRR



$VN_{0.7}O_{0.45}$: VN ratio after ENRR for 1 h at < -0.2 V stabilizes at 0.54

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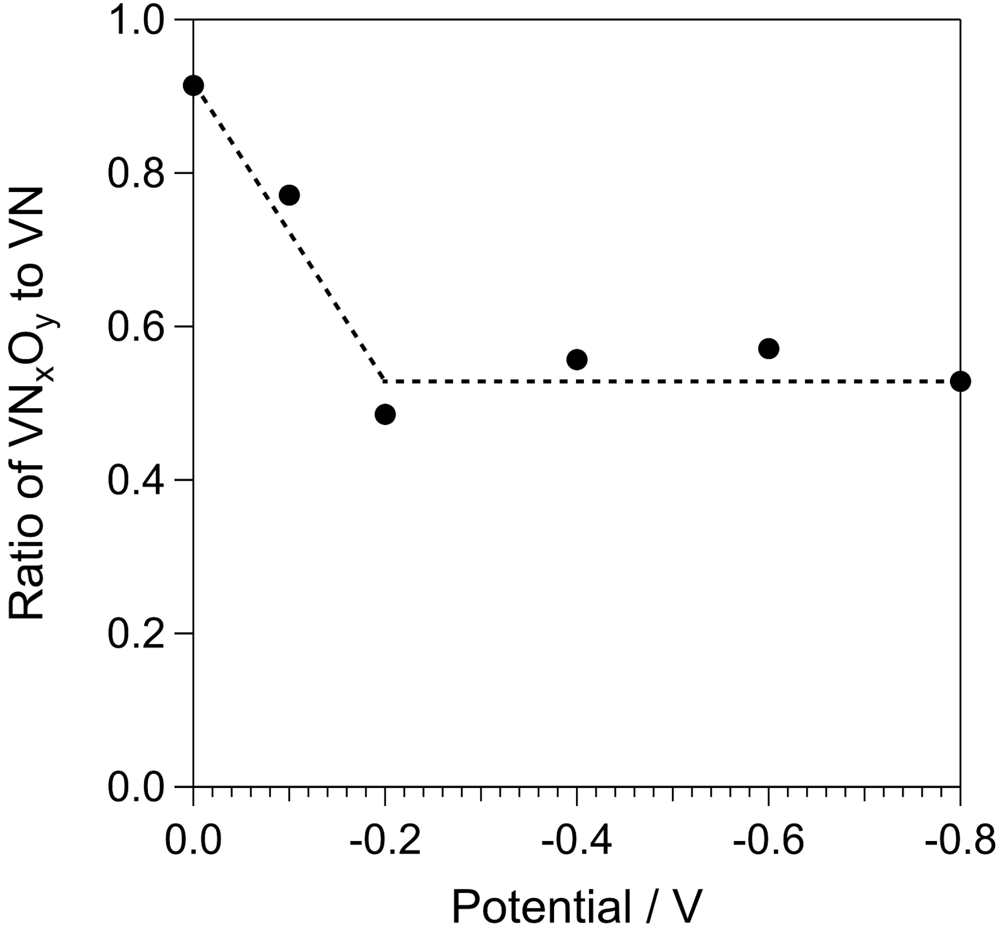
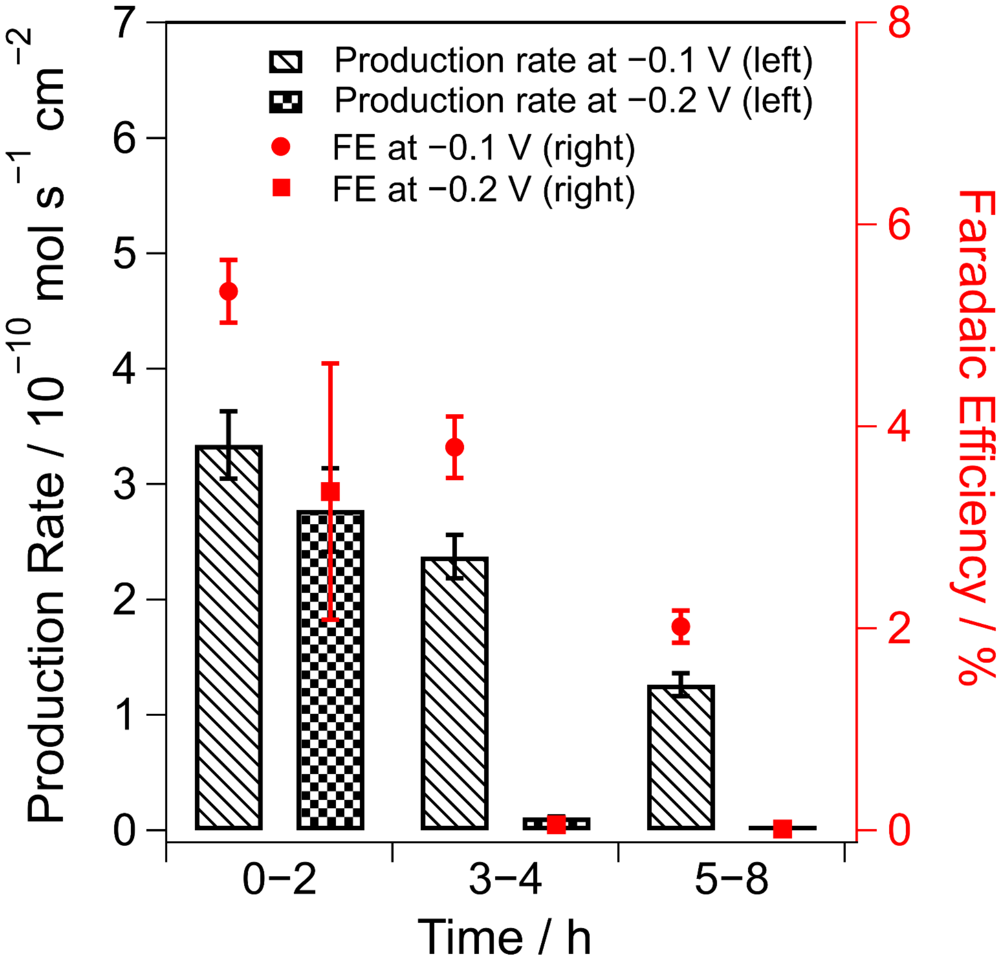
XPS of VN Catalysts after ENRR





$VN_{0.7}O_{0.45}$: VN ratio after ENRR for 1 h at < -0.2 V stabilizes at 0.54

Almost no ammonia is produced after ENRR for 2 h at < -0.2 V

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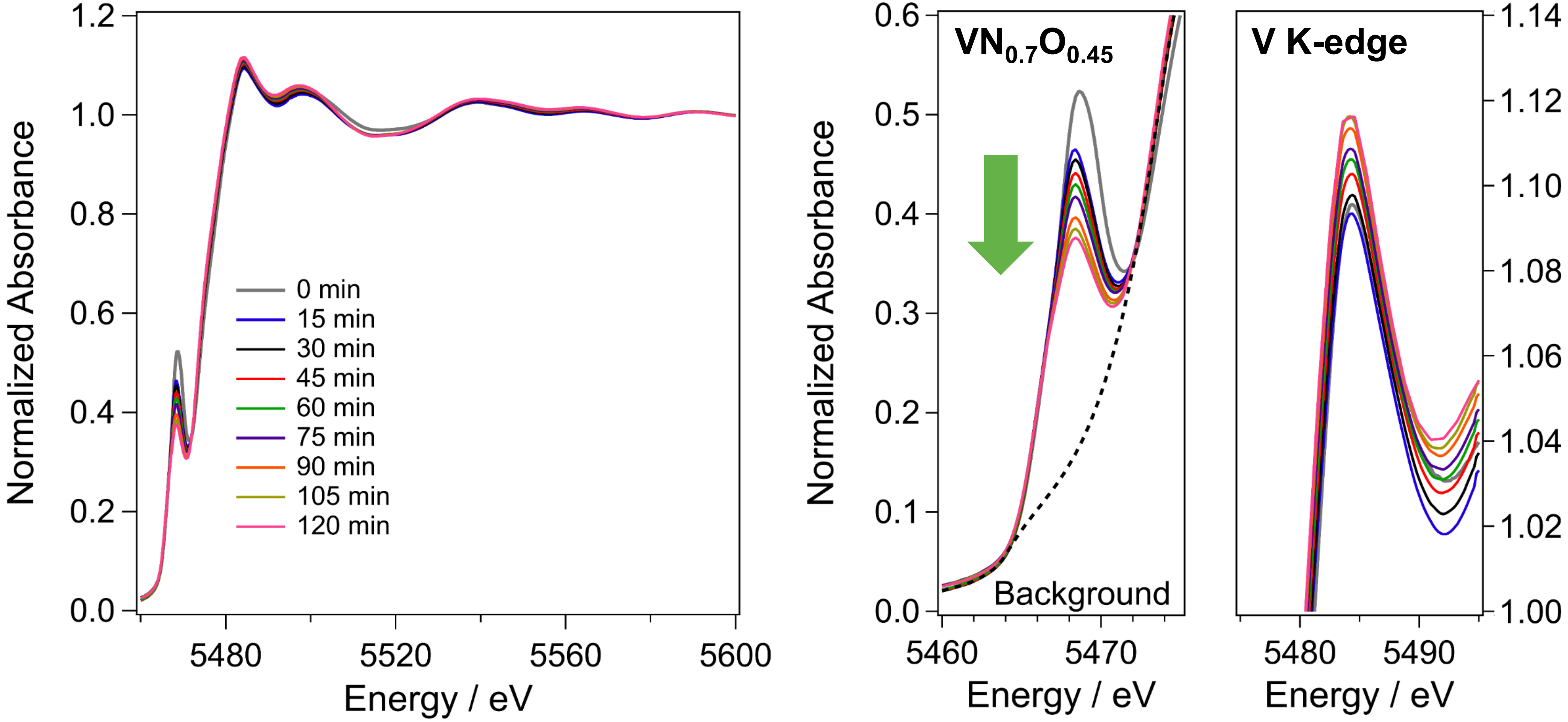
Operando XAS of VN during ENRR



$VN_{0.7}O_{0.45}$ is consumed during ENRR at -0.1 V

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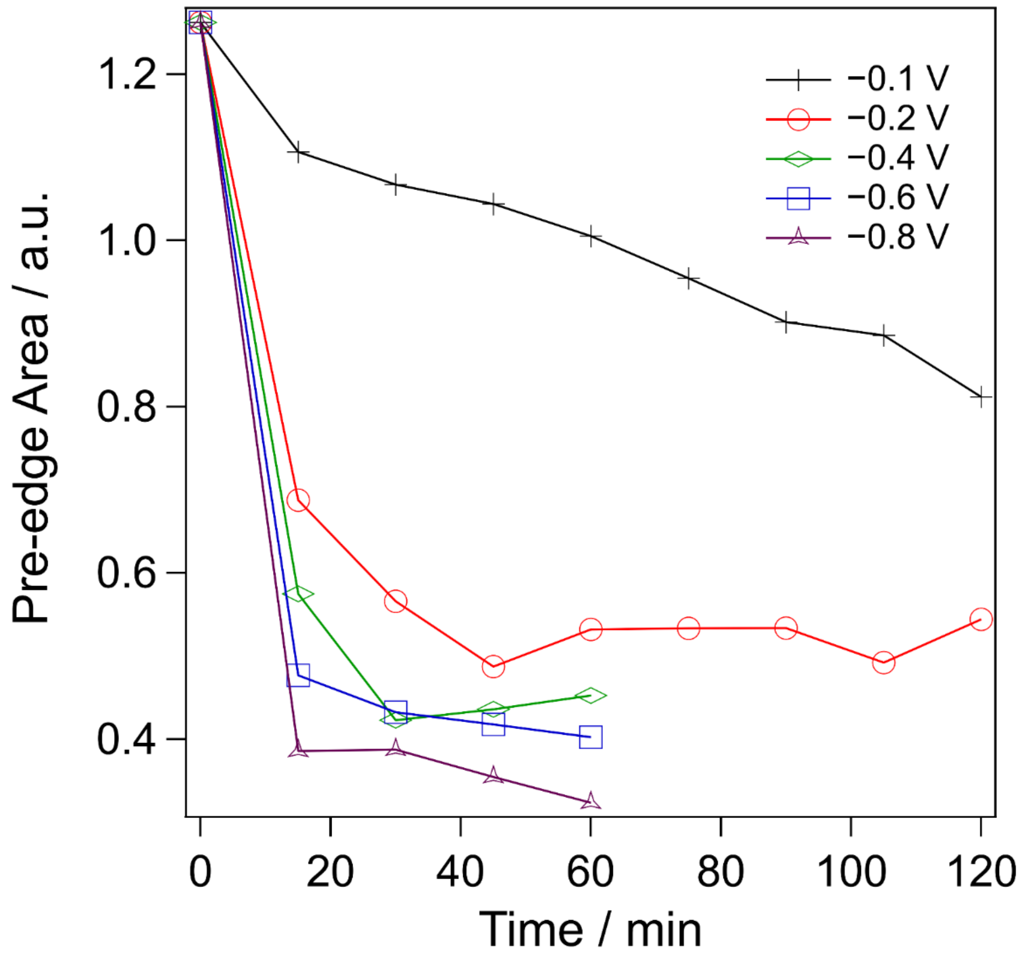
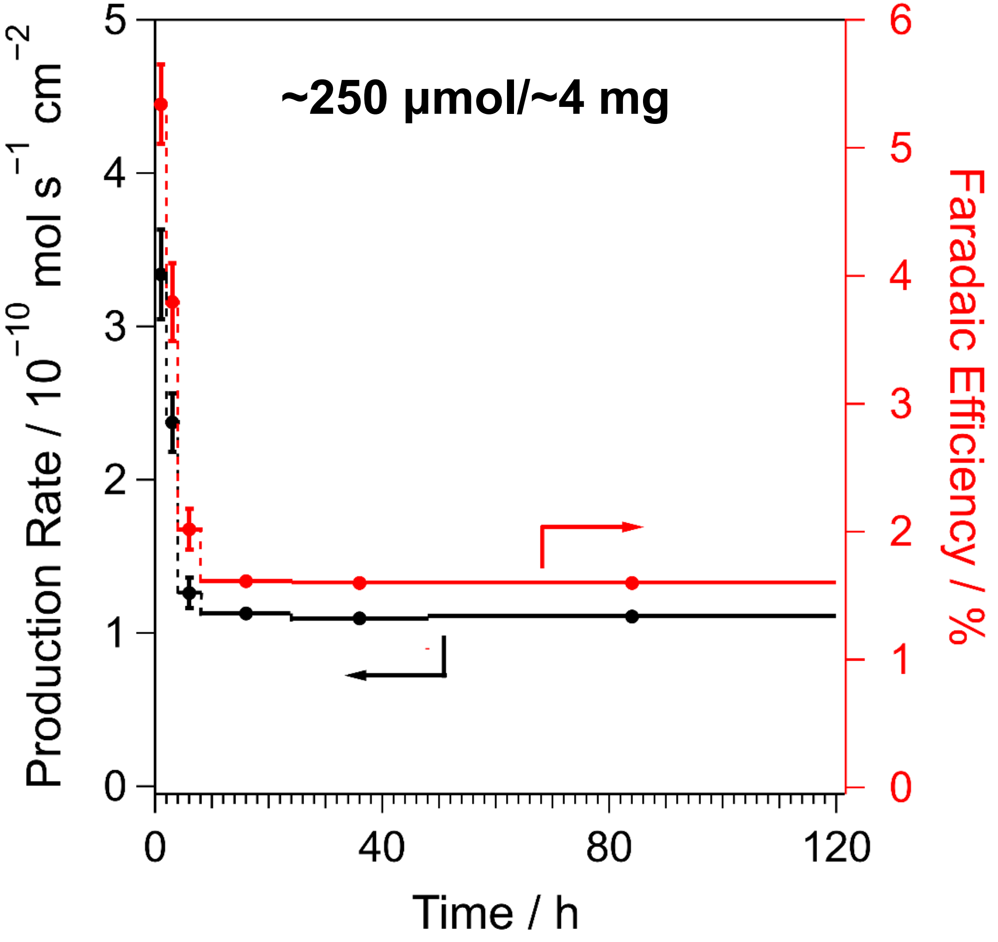
Operando XAS of VN during ENRR





- The consumption rate of $VN_{0.7}O_{0.45}$ is slower at -0.1 V
- Similar and stable amount of $VN_{0.7}O_{0.45}$ is reached in < 1h at < -0.2 V

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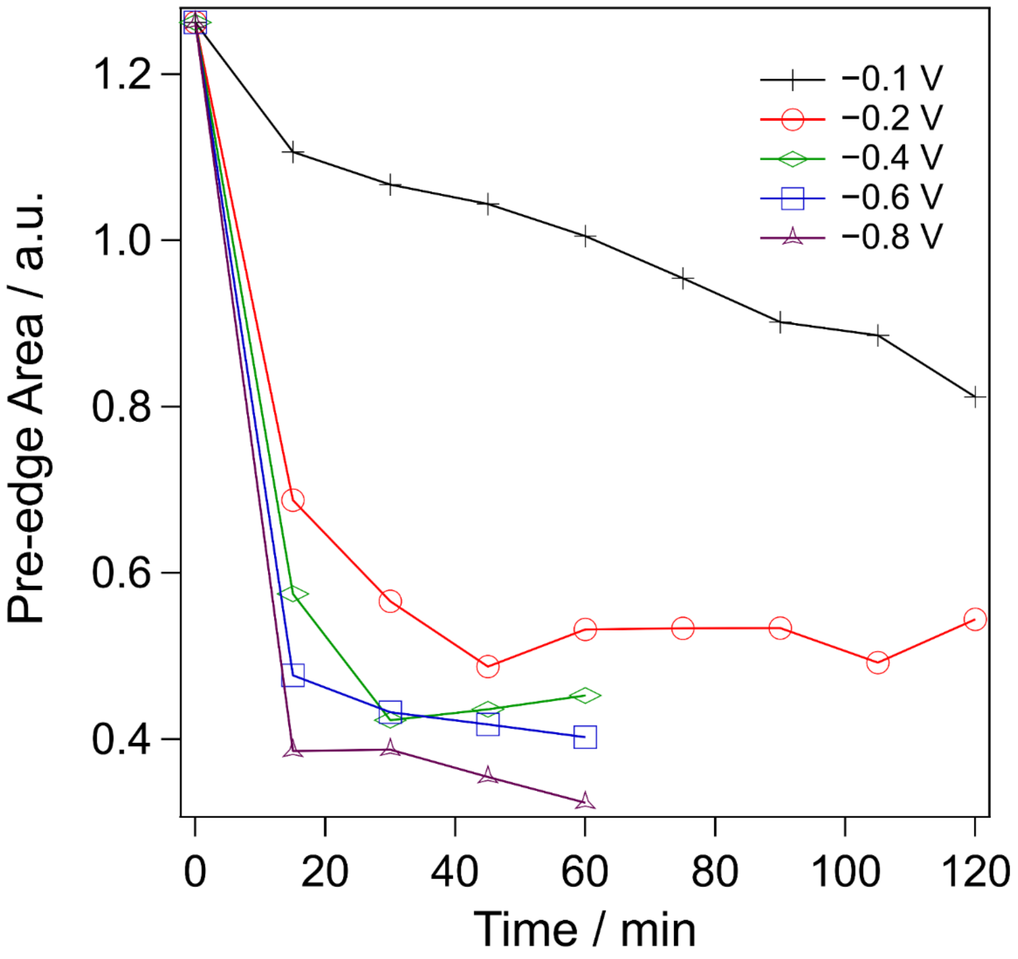
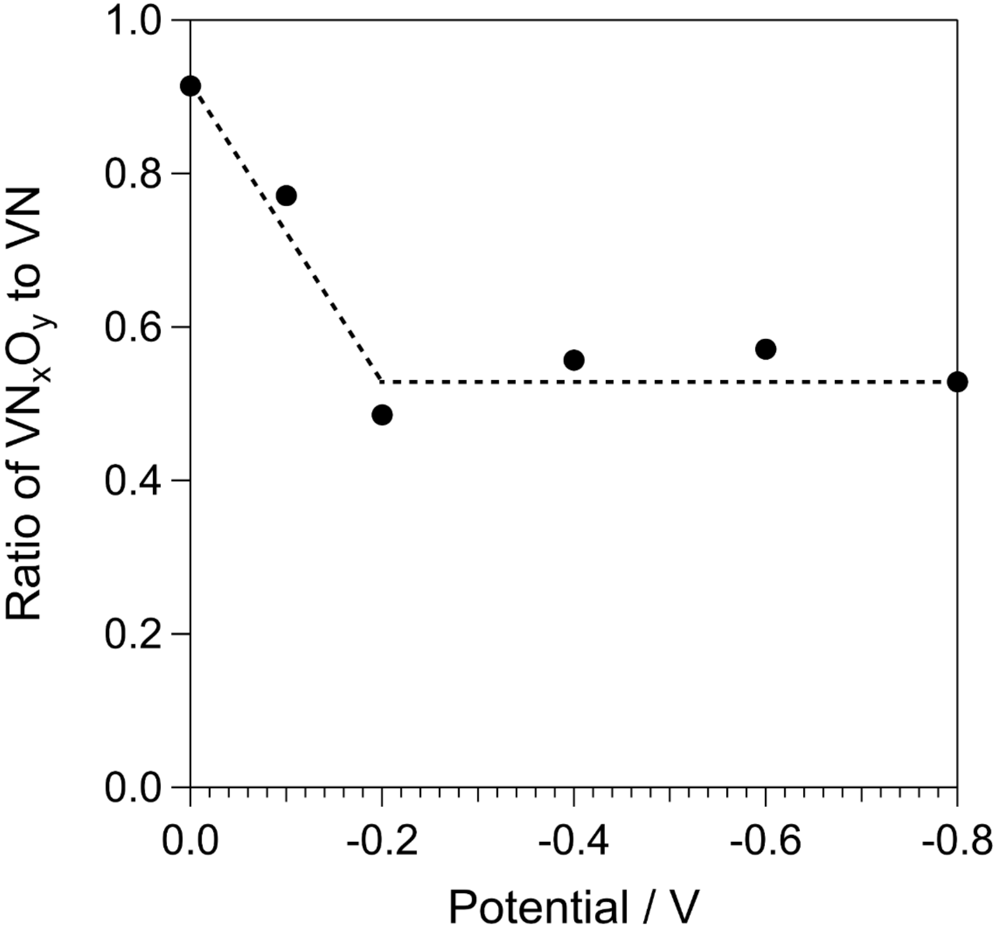
Operando XAS of VN during ENRR





$VN_{0.7}O_{0.45}$ is likely the active phase for ENRR

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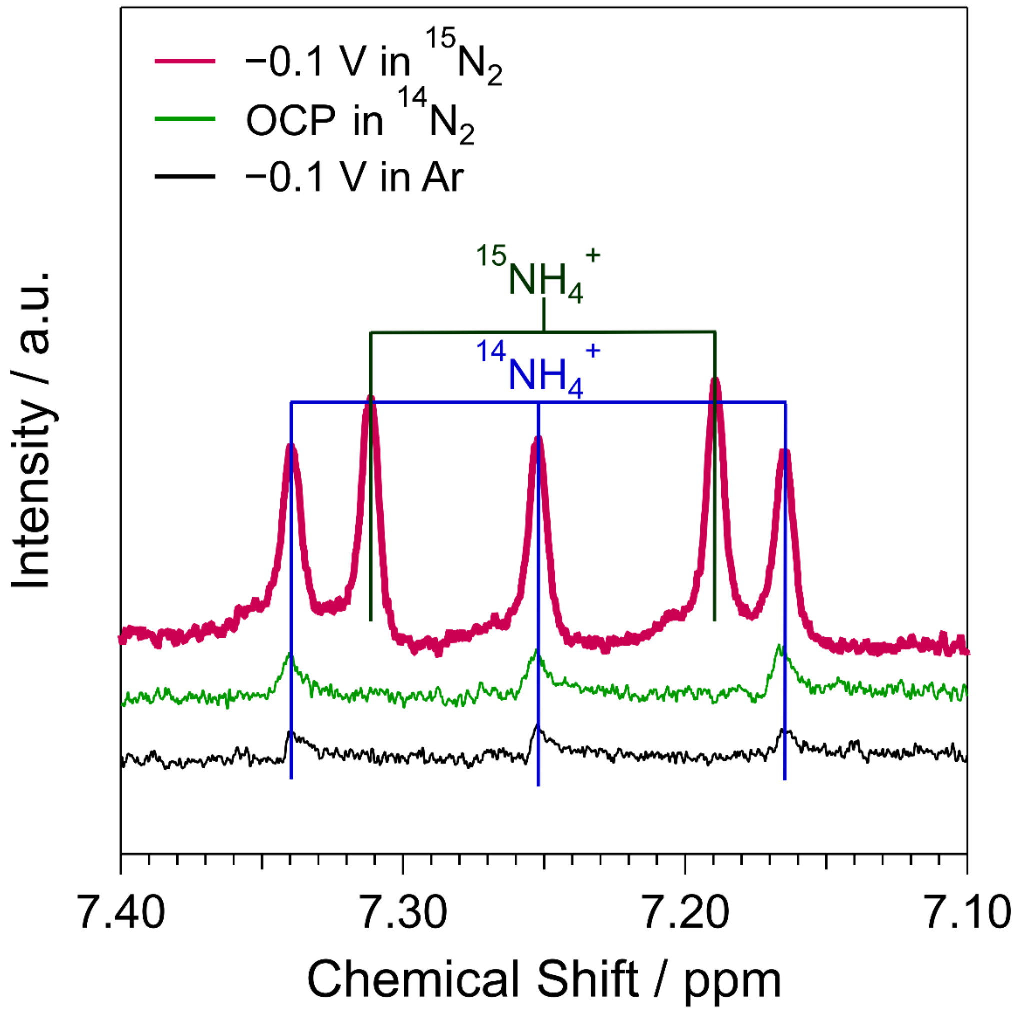
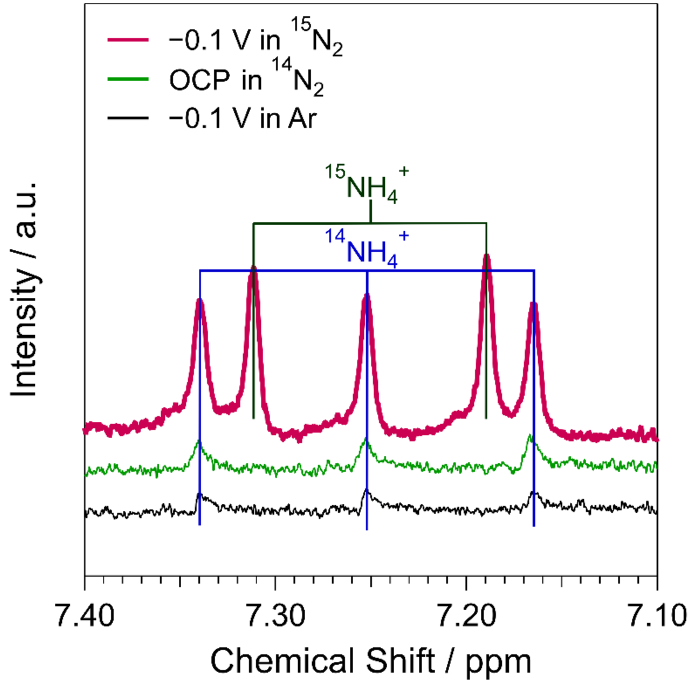
ENRR Occurs via the Mar-van Krevelen Mechanism

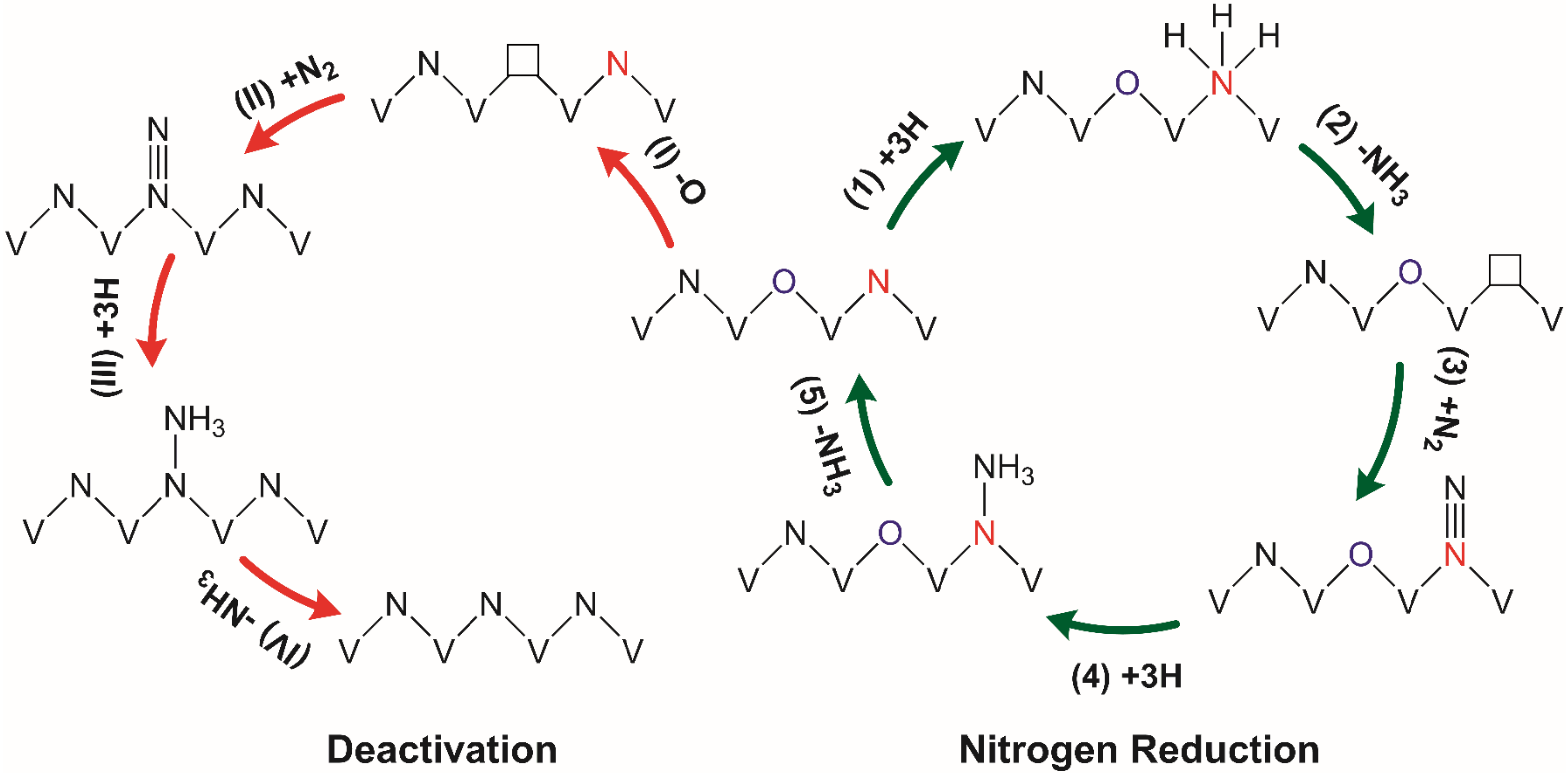


ENRR with $^{15}N_2$ as feed on VN produces both $^{14}NH_3$ and $^{15}NH_3$, indicating the participation of surface N atoms on the catalyst

Yang et al. *J. Am. Chem. Soc.* **2018**, *140*, 13387−13391

ENRR Occurs via the Mar-van Krevelen Mechanism





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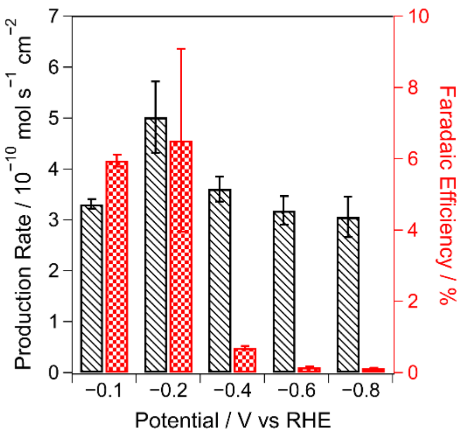
Conclusion

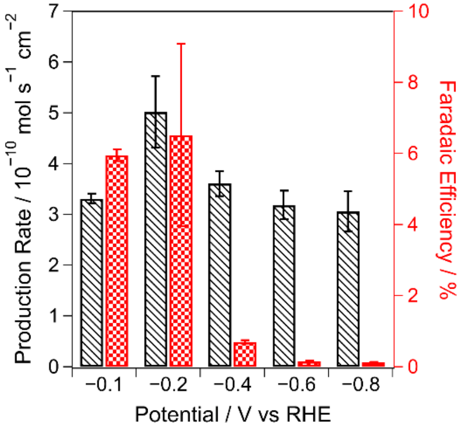
1. VN is an Active, Selective and Stable ENRR Catalyst

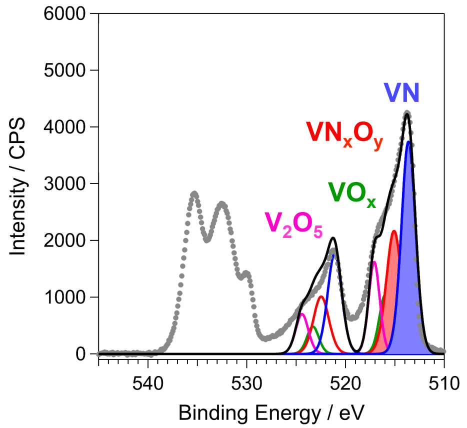


Conclusion

1. **VN is an Active, Selective and Stable ENRR Catalyst**

2. **The active phase is identified to be $VN_{0.7}O_{0.45}$**



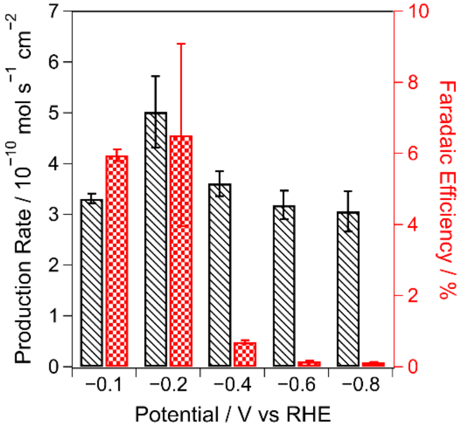


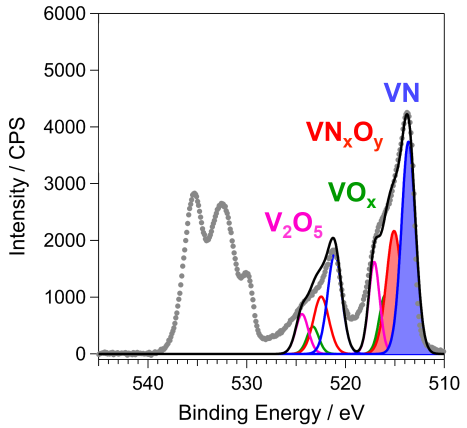
Conclusion

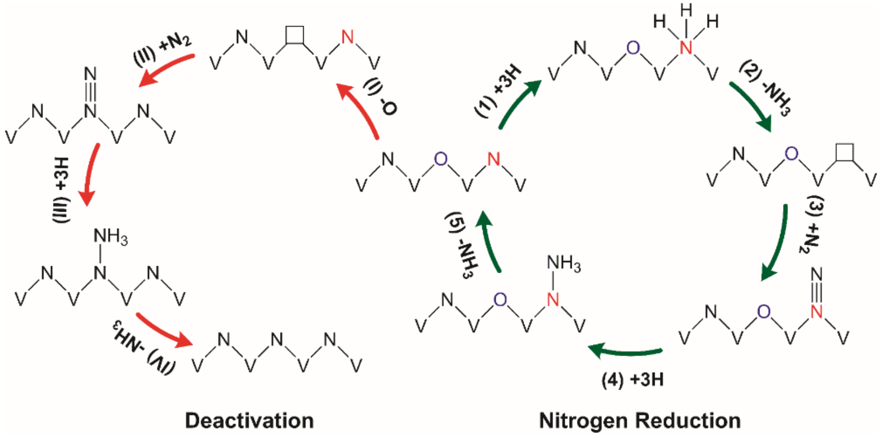
1. **VN is an active, selective and stable ENRR Catalyst**

2. **The active phase is identified to be $VN_{0.7}O_{0.45}$**

3. **ENRR occurs via the Mar-van Krevelen mechanism and the consumption of $VN_{0.7}O_{0.45}$ causes the deactivation**







Acknowledgement

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Collaborators

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Dr. Eli Stavitski

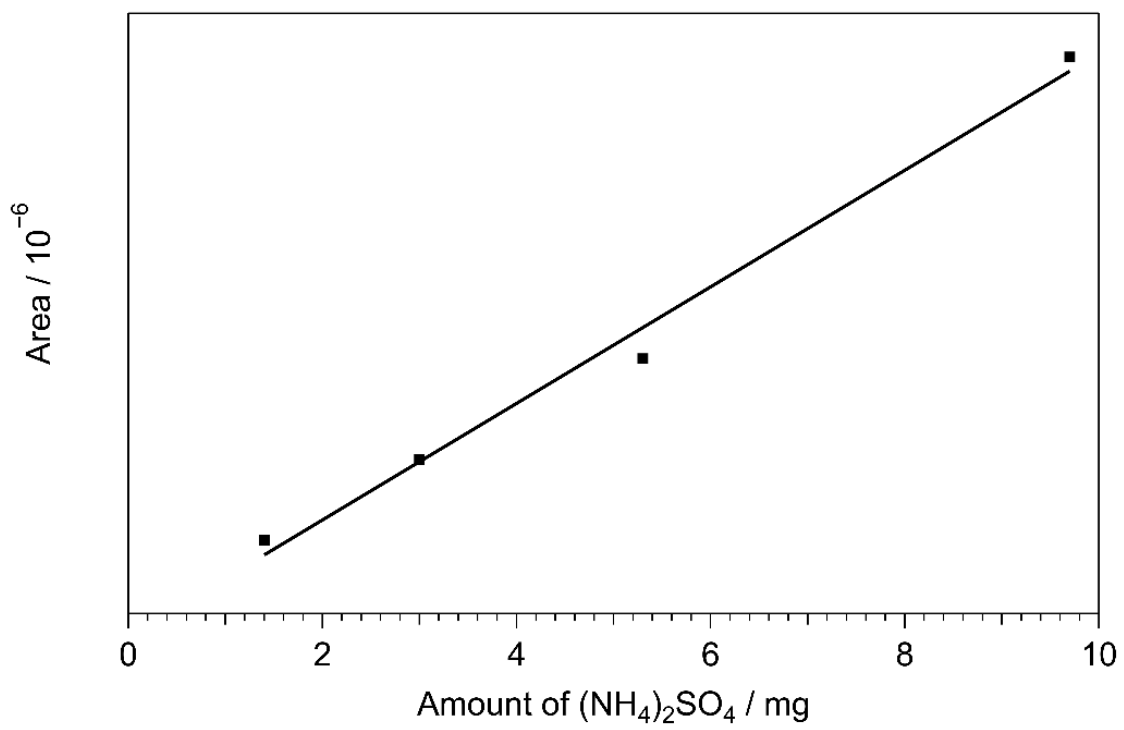
Dr. Klaus Attenkofer

U.S. DEPARTMENT OF ENERGY

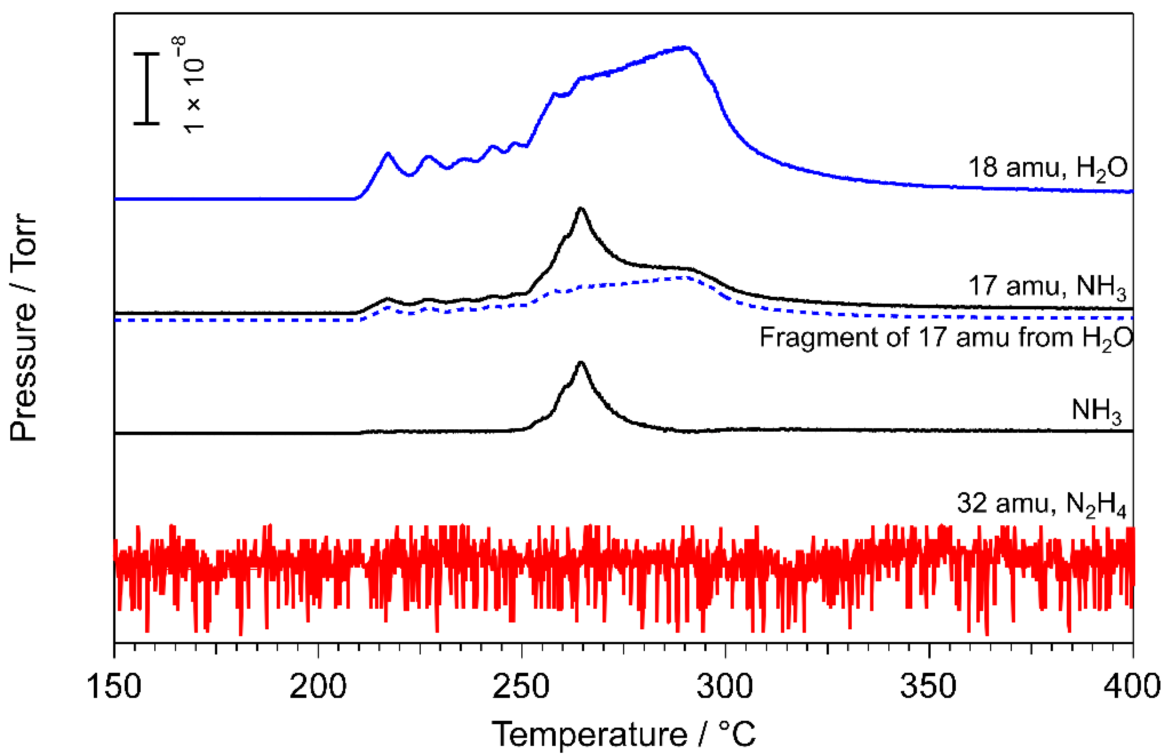
Thank you!

TPD-MS Quantification Agrees with Nessler's Method

Calibration



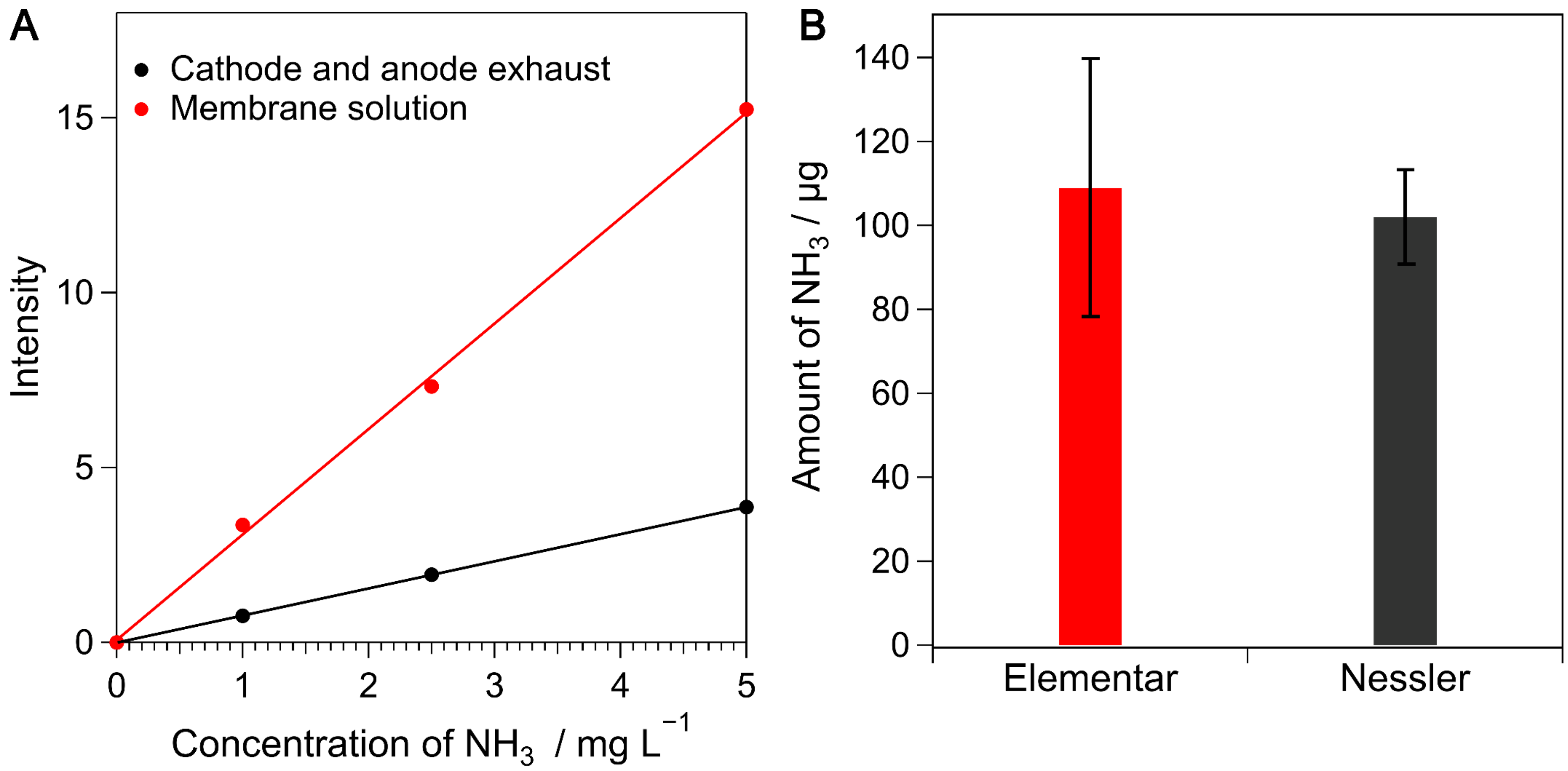
TPD-MS



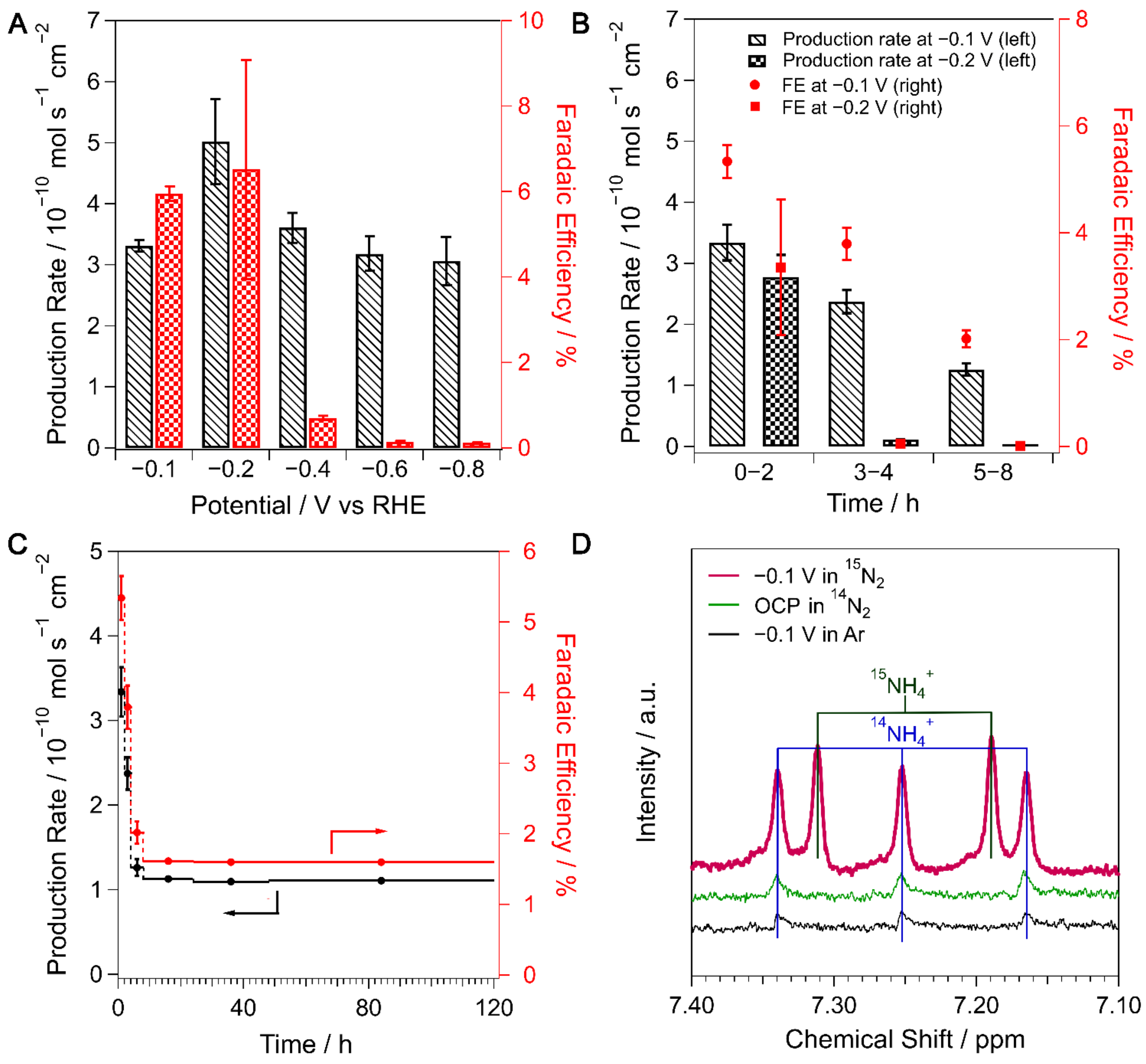
Amount of ammonia quantified by the Nessler's method and TPD-MS are 3.2 mg and 2.9 mg, respectively

ENRR on VN at -0.1 V for 120 h

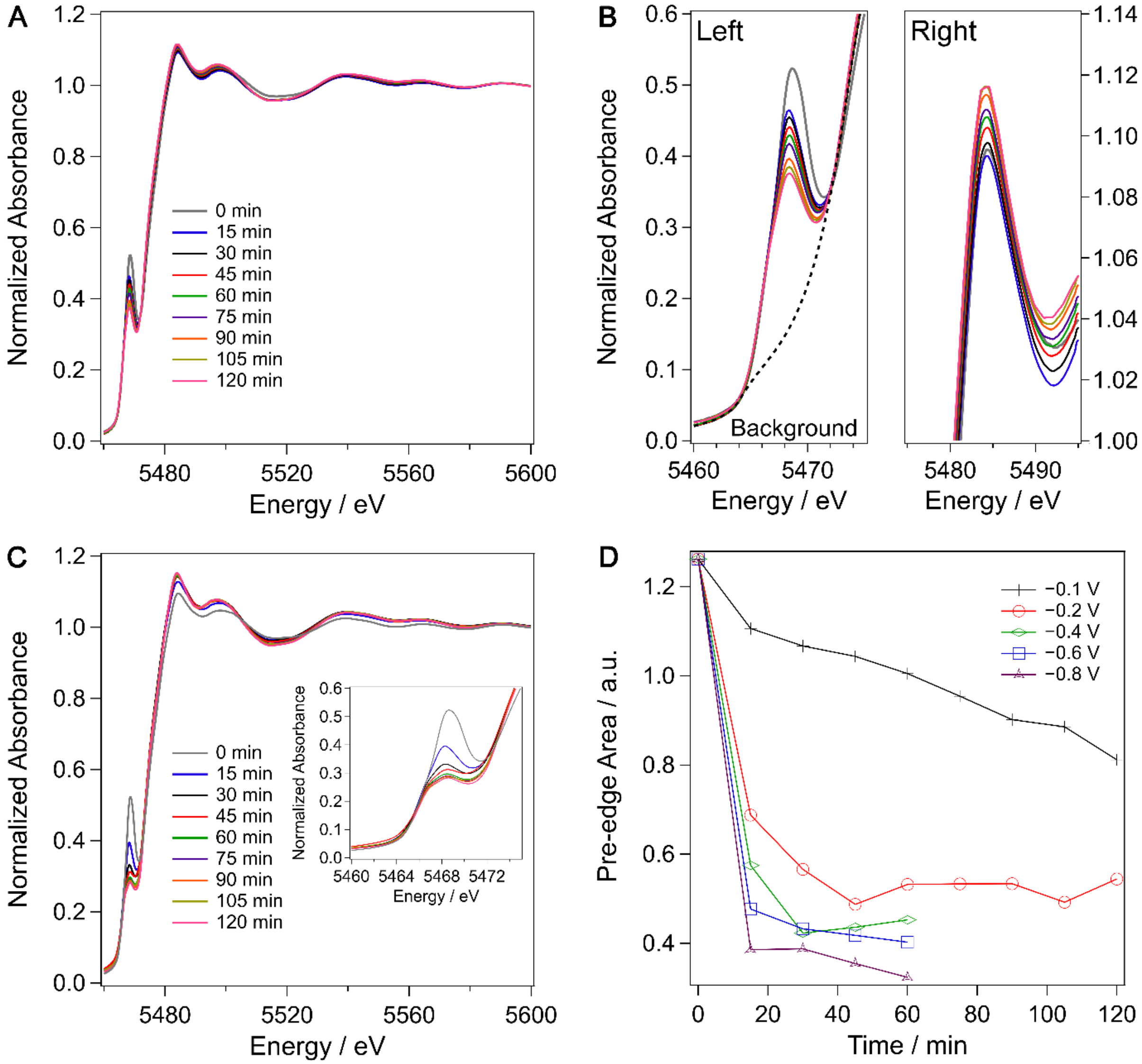
Elementar Analysis Enables Accurate Quantification of Produced Ammonia



ENRR at OCP, the Elementar results were consistent to Nessler results



A
Production Rate / 10^-10 mol s^-1 cm^-2
Faradaic Efficiency / %
Potential / V vs RHE
−0.1
−0.2
−0.4
−0.6
−0.8
B
Production rate at −0.1 V (left)
Production rate at −0.2 V (left)
FE at −0.1 V (right)
FE at −0.2 V (right)
Time / h
0−2
3−4
5−8
C
Time / h
D
−0.1 V in 15N2
OCP in 14N2
−0.1 V in Ar
15NH4+
14NH4+
Intensity / a.u.
Chemical Shift / ppm



A
Normalized Absorbance
Energy / eV
0 min
15 min
30 min
45 min
60 min
75 min
90 min
105 min
120 min
B
Left
Right
Background
Normalized Absorbance
Energy / eV
C
Normalized Absorbance
Energy / eV
D
Pre-edge Area / a.u.
Time / min
−0.1 V
−0.2 V
−0.4 V
−0.6 V
−0.8 V

Turnover Number (TON) in ENRR

1. Based on the Elementar analysis and TGA results, the total N and V contents in the catalysts was 15.51 wt% and 58.5 wt%, respectively.

2. Since there was 2.5 mg of the catalysts on carbon paper, the amounts of $VN_{0.7}O_{0.45}$ (d) and VN phase (e) were determined to be 3.5 μmol and 25.2 μmol, respectively.

$$0.7 \times d + e = \frac{2.5\times10^{-3}\times15.51\%}{14}$$

$$d + e = \frac{2.5\times10^{-3}\times58.5\%}{50.9}$$

3. XAS results suggest that the accessible amount of $VN_{0.7}O_{0.45}$ was 57.8%, therefore, the TON of the catalysts within 120 h is:

$$\frac{253.1\ \mu mol}{3.5 \times 0.7\ \mu mol \times 57.8\%} = 179$$

Overall TON

4. XAS results suggest that 35.7% of $VN_{0.7}O_{0.45}$ was converted to VN at −0.1 V for 2 h. Thus, the total amount of active nitrogen atoms in the catalysts after 4 h was:

$$3.5 \times (57.8\% - 35.7\%) \times 0.7\ \mu mol = 0.54\ \mu mol$$

5. Since the total amount of ammonia produced at −0.1 V from 5 to 120 h was determined to be 232.5 μmol. the turnover number (TON) of the catalysts at steady state (5−120 h) was determined to be:

$$\frac{232.5\ \mu mol}{0.54\ \mu mol} = 431$$

Steady State TON