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

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N mass balance enables the reliably quantification of produced ammonia.

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

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


~250 µmol/~4 mg
VN is an Active, Selective and Stable ENRR Catalyst

Key questions:
• What is the active phase in ENRR?
• How does VN deactivate?

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can be maintained for 120 h

~250 µmol/~4 mg
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
Based on the ratio of V 2p and N 1s bands assigned to VN$_x$O$_y$, and assuming a +3 oxidation state of V, the composition of the oxynitride is VN$_{0.7}$O$_{0.45}$

VN\textsubscript{0.7}O\textsubscript{0.45} : VN ratio on the fresh VN is \(~0.91\)

XPS of VN Catalysts before ENRR

V_{N_{0.7}O_{0.45}}: VN ratio on the fresh VN is \( \sim 0.91 \)

How does the surface composition change during ENRR?
VN$_{0.7}$O$_{0.45}$: VN ratio decreases to 0.77 after ENRR at −0.1 V for 1 h
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

$\text{VN}_{0.7}\text{O}_{0.45}$: 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

Operando XAS of VN during ENRR

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

**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

Operando XAS of VN during ENRR

$\text{VN}_{0.7}\text{O}_{0.45}$ is likely the active phase for ENRR

ENRR Occurs via the Mar-van Krevelen Mechanism

ENRR with $^{15}\text{N}_2$ as feed on VN produces both $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$, indicating the participation of surface N atoms on the catalyst.
ENRR Occurs via the Mar-van Krevelen Mechanism

Conclusion

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2. The active phase is identified to be VN$_{0.7}$O$_{0.45}$
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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

Collaborators

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Thank you!
TPD-MS Quantification Agrees with Nessler’s Method

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
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.

   \[
   \begin{align*}
   0.7 \times d + e &= \frac{2.5 \times 10^{-3} \times 15.51}{14} \\
   d + e &= \frac{2.5 \times 10^{-3} \times 58.5}{50.9}
   \end{align*}
   \]

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**