Nickel-Nitrogen-Carbon (NiNC) Catalysts for the Ammonia Oxidation Reaction

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Motivation & Approach

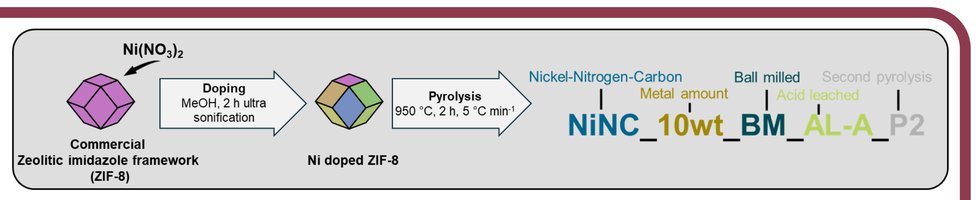
- NH_3 has significant potential as an energy carrier for the storage and transport of renewable H_2 [1]
  - Electrochemical production and decomposition of NH_3 needed for efficient energy storage capabilities
  - Nickel promising non-noble metal for electrochemical oxidation of NH_3[2]
- Homogeneous Ni-N-complexes showed activity for ammonia oxidation reaction (AOR)[3]

This Study:

- Synthesis and characterization of heterogenous nickel-nitrogen-carbon (NiNC) catalysts
- Challenges: slow kinetics, carbon corrosion, poisoning of active sites

Results – ZIF-8 based NiNCs

- Metal organic frameworks (MOF) based synthesis with ZIF-8 and Ni and pyrolysis at 950 °C for 2 h[4]
- Systematic study of nickel loading to investigate optimal metal content without metallic particle formation
- Electrochemical screening for AOR activity



Physical Characterization

- Amorphous carbon for most samples
- Nanoparticle & carbon nanotube (CNT) formation at high Ni loadings (> 10 wt%) (Fig. 1 & 2)

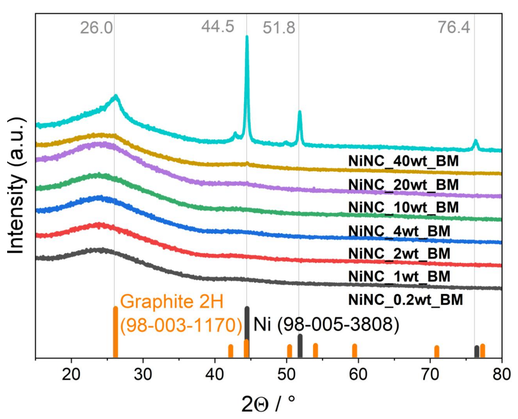


Figure 1: XRD of NiNCs with varied Ni content.

- Samples retain ZIF-8 morphology at low Ni loadings (< 4 wt%)
- Sample NiNC_10wt_BM chosen for electrochemical evaluation
  - No Ni nanoparticle & carbon nanotube formation

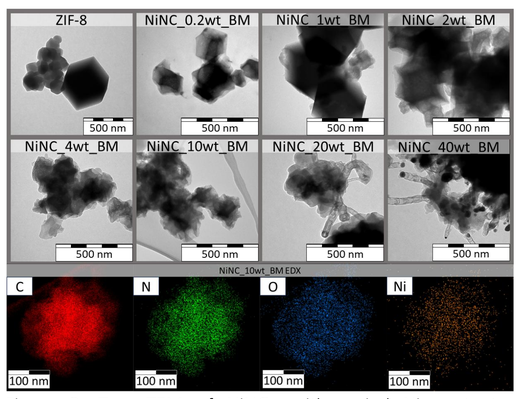


Figure 2: Top: TEM of NiNCs with varied Ni content. Bottom: EDX of NiNC_10wt.

Electrochemical Characterization

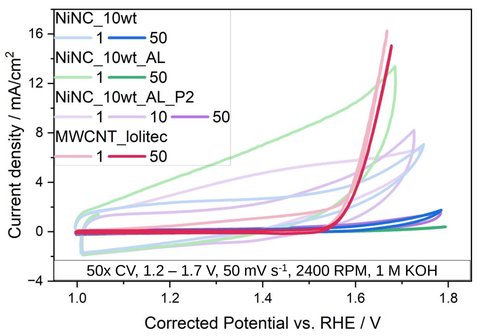


Figure 3: CVs of NiNC_10wt with different synthesis variations.

- Cycling at AOR/OER potentials (Fig. 3) resulted in a decrease of 76 % in current density over 50 cycles, subsequent acid leaching resulted in an decrease of 97% of current density
  → Carbon corrosion assumed
- Acid leaching (AL) and second pyrolysis (P2) failed to provide long-term stability
- Addition of NH_3 (Fig. 4)
  - Increase of current density for untreated sample
  - Decrease of current density after three cycles
- NH_3 might influence initial catalyst activity for OER
- **Negligible AOR activity**
- **→ Avoiding carbon corrosion by use of carbon nanotubes**

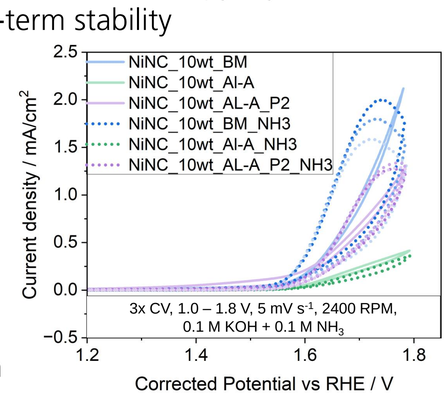
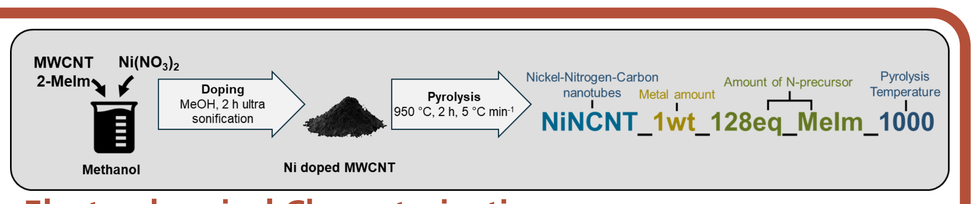


Figure 4: CVs with and without addition of NH_3.

Results – MWCNT based NiNCNTs

- Multiwalled carbon nanotubes used as a carbon support, pyrolyzed with Ni & N precursors
- Systematic investigation of Ni–N and Ni–C coordination environments by variation of the pyrolysis temperature (600 – 1000 °C)



Physical Characterization

- Formation of metallic Ni nanoparticles at higher pyrolysis temperatures (>800 °C) (Fig. 5 & 6)

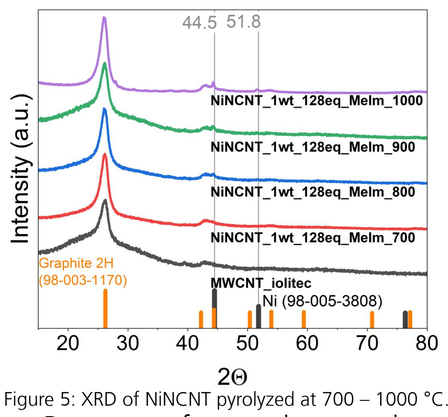


Figure 5: XRD of NiNCNT pyrolyzed at 700 – 1000 °C.

- Presence of amorphous carbon

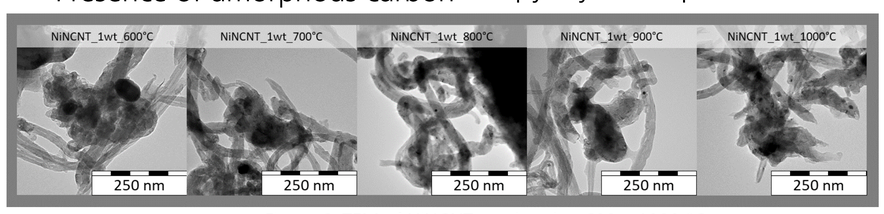


Figure 6: TEM of NiNCNT pyrolyzed at 600 – 1000 °C

- Metallic Ni (Ni^0) is not detected at its characteristic binding energy, indicating encapsulation of Ni nanoparticles at elevated temperatures (>800 °C) (Fig. 5 & 7)
- At lower pyrolysis temperatures Ni is predominantly surface-exposed
- Overall N content and pyridinic N fraction decrease with increasing pyrolysis temperature

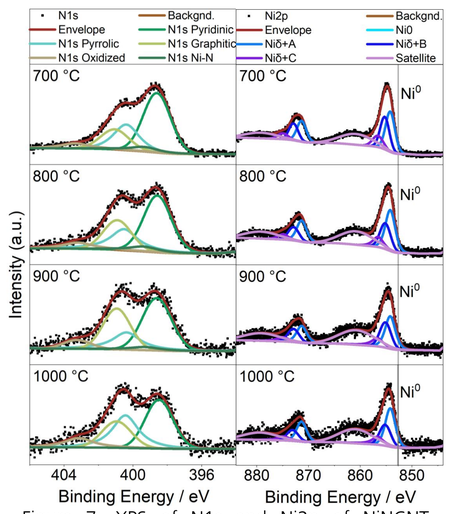


Figure 7: XPS of N1s and Ni2p of NiNCNT pyrolyzed at 700 – 1000 °C.

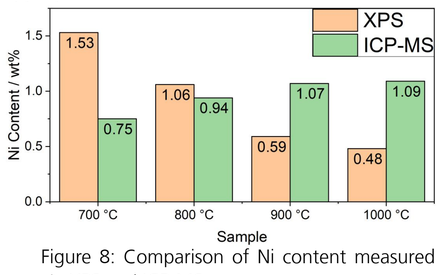


Figure 8: Comparison of Ni content measured via XPS and ICP-MS.

Electrochemical Characterization

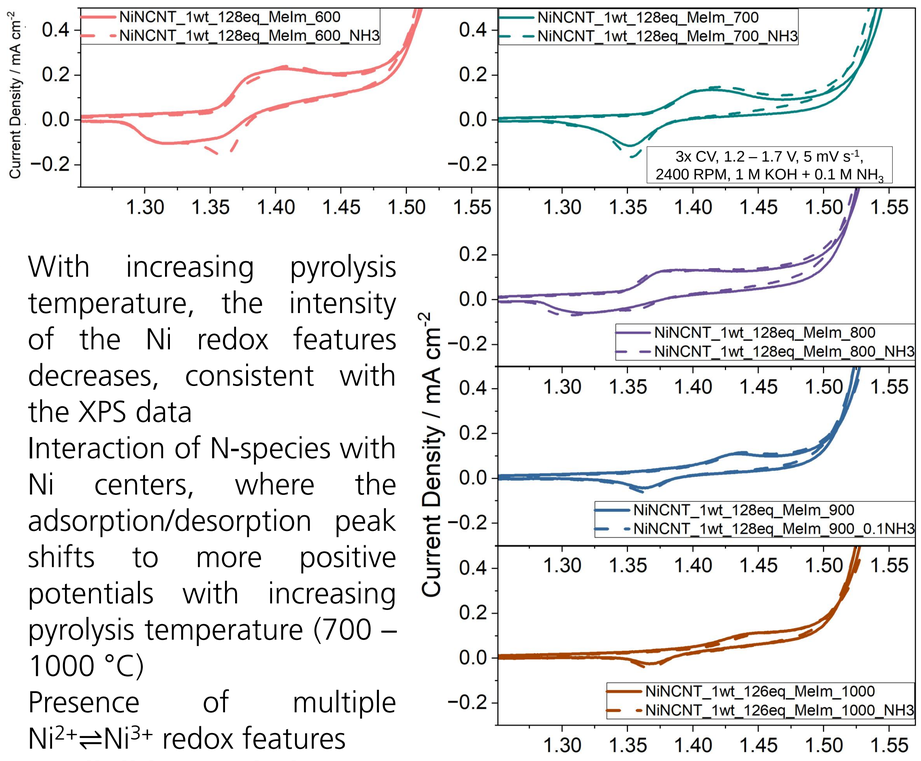


Figure 9: CVs of NiNCNT pyrolyzed at 600 - 1000 °C with and without addition of NH_3.

- With increasing pyrolysis temperature, the intensity of the Ni redox features decreases, consistent with the XPS data
- Interaction of N-species with Ni centers, where the adsorption/desorption peak shifts to more positive potentials with increasing pyrolysis temperature (700 – 1000 °C)
- Presence of multiple $Ni^{2+} \rightleftharpoons Ni^{3+}$ redox features
- **Negligible catalytic AOR activity of all samples**

Summary

- Ni–N–C catalysts were prepared by pyrolysis of Ni-doped ZIF-8 (NiNC) and Ni/MWCNT composites (NiNCNT)

NiNC:

- High Ni loadings induce metallic Ni nanoparticle and CNT formation
- Loses 76% of its current density over 50 cycles at AOR/OER potentials; acid leaching and re-pyrolysis do not enhance stability → No AOR activity

NiNCNT:

- Metallic Ni nanoparticles formed at 800–1000 °C (XRD, TEM) but are not detected as Ni^0 by XPS, indicating encapsulation in a carbon shell
- Ni is predominantly surface-exposed at lower T (< 800 °C)
- Commercial MWCNTs exhibit good electrochemical stability
- Ni^{2+}/Ni^{3+} redox features decrease in intensity with pyrolysis temperature
- NH_3 interacts with Ni centers, with its desorption peak shifting to more positive potentials → but no AOR activity

Outlook

- Focus on other Ni-type catalysts for AOR
  - Using MWCNTs as support for different Ni containing compounds for AOR (e.g. NiS)
- Quantification of ammonia and reaction products via UV-Vis, in-situ EC-MS and IC

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This publication was created as part of the research program "Transforming the Energy System Lower Saxony" (TEN.efzn) at the Energy Research Center of Lower Saxony (efzn).
Funded by zukunft.niedersachsen, the joint science funding program of the Lower Saxony Ministry of Science and Culture and the Volkswagen Foundation
Grant Number: 11-76251-2884/2024 (ZN4464)
The authors acknowledge the Electron and Light Microscopy Service Unit of the School of Mathematics and Science of the Carl von Ossietzky University for the use of the imaging facilities. (INST 184/ 106-1 FUGG)
Special thanks to Jana Ewert for ICP-MS measurements.