Nickel-Zinc Symposium - Military Power Sources Committee, Virtual Meeting

Nanostructured α-$Ni(OH)_2$ Cathodes for High Energy Density Rechargeable Nickel-Zinc Batteries

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Nickel–Zinc Alkaline Batteries: Benefits and Opportunities

Major safety issues with Li-ion

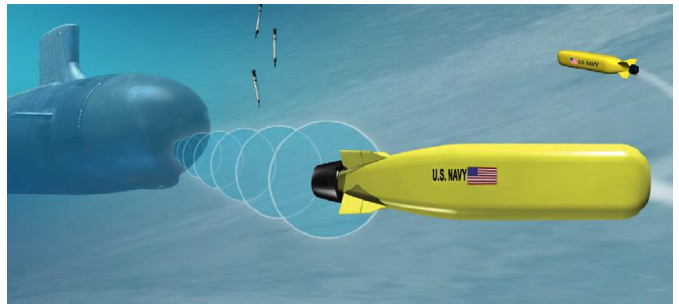
- Overcharging, battery damage, fabrication flaws ⇒ cell failure
- Cell failures ⇒ thermal runaway ⇒ ignition & propagation



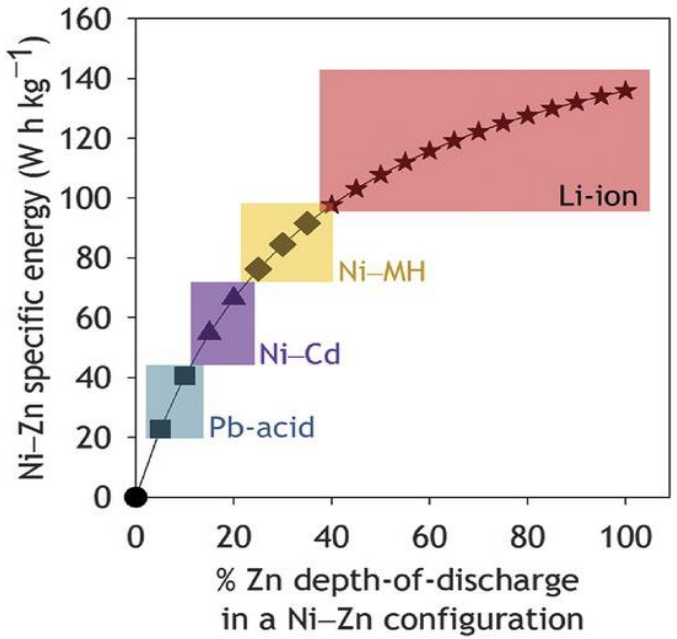


Cooper, A., Dreamliners grounded globally due to fire risk. *CNN* 2013

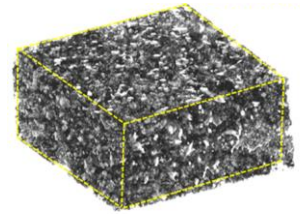
Safety issues of Li-ion batteries: problematic for personnel and military platforms



$$2\,NiOOH_{(s)} + Zn + H_2O_{(l)} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_{2\,(s)} + ZnO_{(s)}$$



Zinc sponge



Developed at U.S. Naval Research Laboratory (NRL)

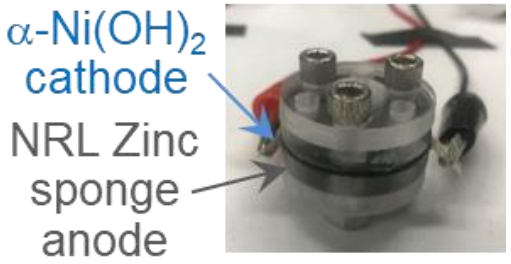
Benefits of Nickel-Zinc batteries

- Aqueous electrolyte
- Zn sponge anodes resolve the poor cyclability resulting from dendritic growth
- Can approach the system-level specific energy Li-ion without wasted space/mass required to mitigate system-failures

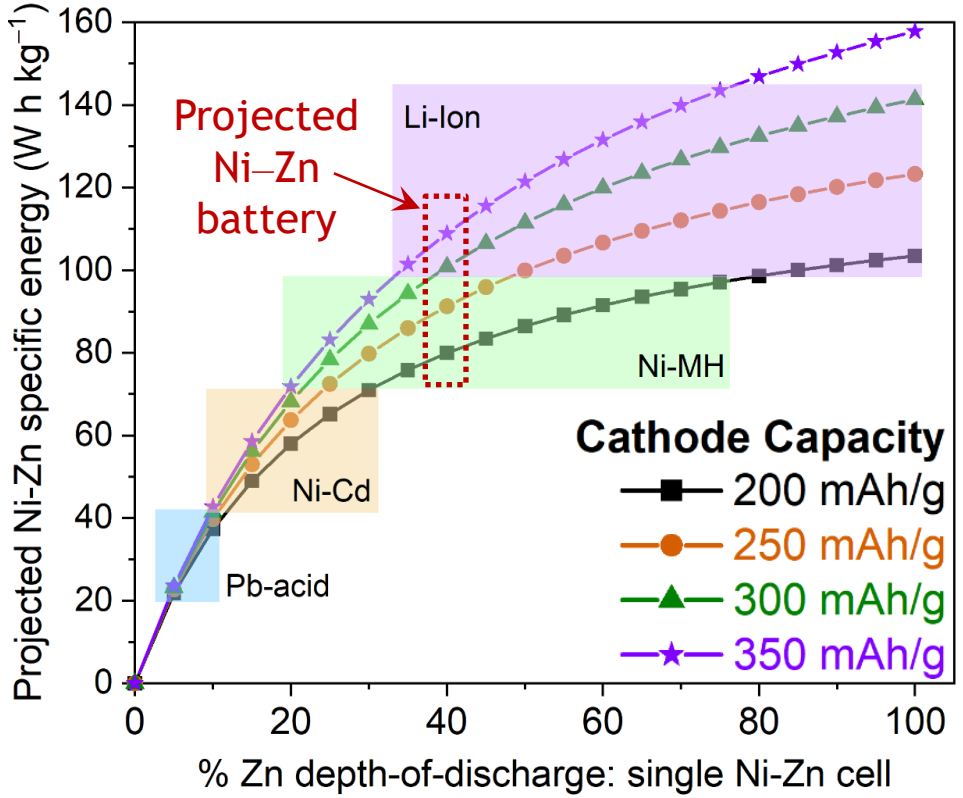
Parker; Chervin; Pala; Machler; Burz; Long; Rolison, *Science* **2017,** *356* (6336), 415-418.
Hopkins; Sassin; Chervin; DeSario; Parker; Long; Rolison, *Energy Storage Materials* **2020,** *27*, 370-376

Motivation for Improved Cathodes for Nickel–Zinc Alkaline Batteries

Nickel cathode that better matches NRL's Zn sponge anode
→ enable *safe*, *high energy density alkaline* Ni–Zn battery



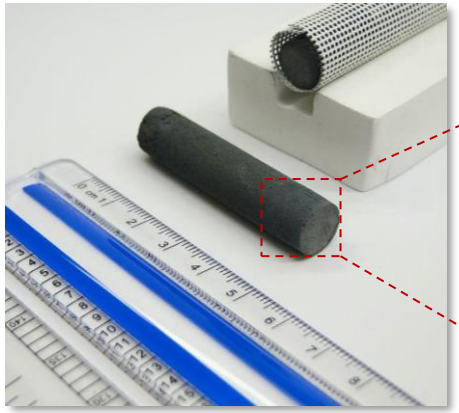
↑ cathode capacity
↑ battery's specific energy
→ Ni–Zn batteries with specific energies in the range of Li-ion



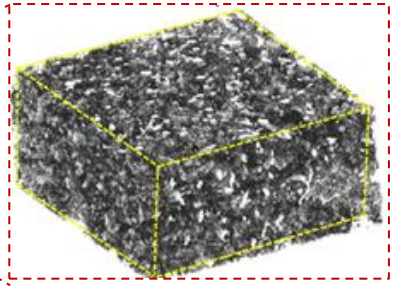
Improved cathodes are needed

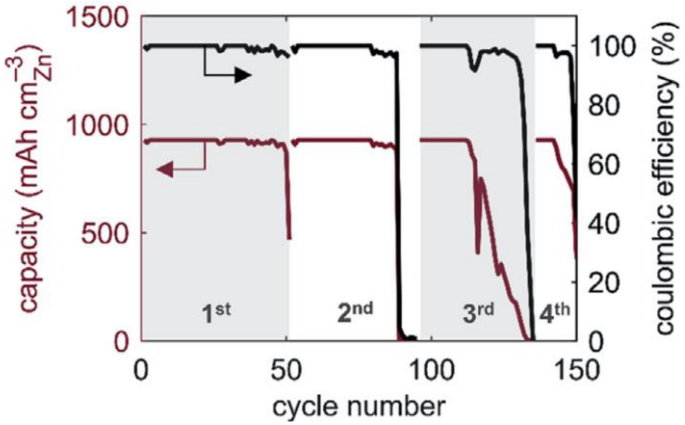
$$2NiOOH_{(s)} + 2H_2O_{(l)} + 2e^- \rightleftharpoons 2Ni(OH)_{2\,(s)} + 2OH^-_{(aq)}$$

Increasing the cathode capacity beyond one e⁻ per Ni would increase the specific energy of practical Ni–Zn batteries



NRL's Zn_{sponge} anode





- Parker, Chervin, Pala, Machler, Burz, Long, Rolison, *Science* **356** (2017) 415
- Ko, Geltmacher, Hopkins, Rolison, Long, Parker, *ACS Appl. Energy Mater.* **2** (2018) 212
- Hopkins, Sassin, Chervin, DeSario, Parker, Long, Rolison, *Energy Storage Mater.* **27** (2020) 370
- Hopkins, Sassin, Parker, Long, Rolison, Zinc-Sponge Battery Electrodes that Suppress Dendrites, *J. Vis. Exp.* (2020) E61770

Alkaline Nickel Hydroxide Cathode Battery Chemistry

β-$Ni(OH)_2$

✓ Industry standard cathode material

✓ Stable in alkaline electrolyte

• 1 e^- theoretical capacity: 289 mAh g^{-1}

× Overcharging → cathode volume expansion

α-$Ni(OH)_2 \cdot nH_2O$

• Hydrated layers of β-$Ni(OH)_2$

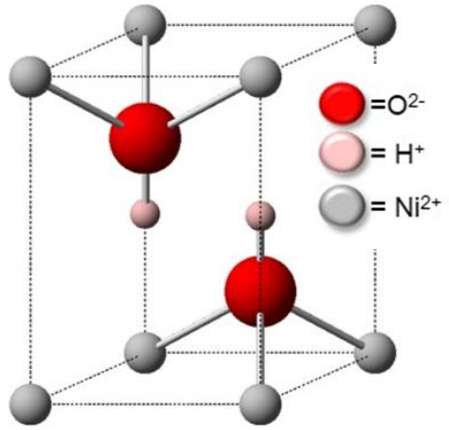
• 1.67 e^- theoretical capacity: 487 mAh g^{-1}

• No volumetric expansion upon overcharge

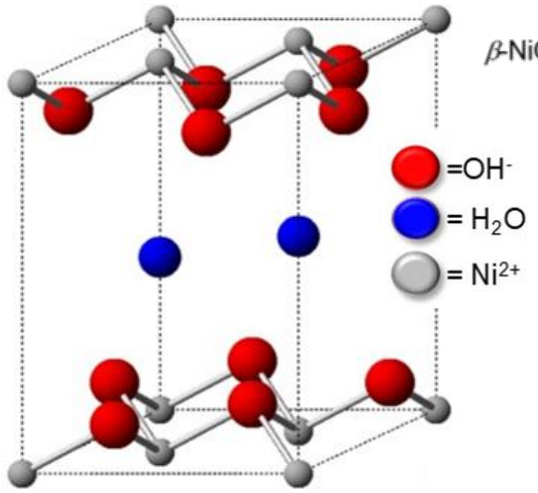
× Unstable in alkaline electrolyte (even without cycling!) → converts to β-$Ni(OH)_2$

→ Requires structural stabilization to access & retain higher capacity

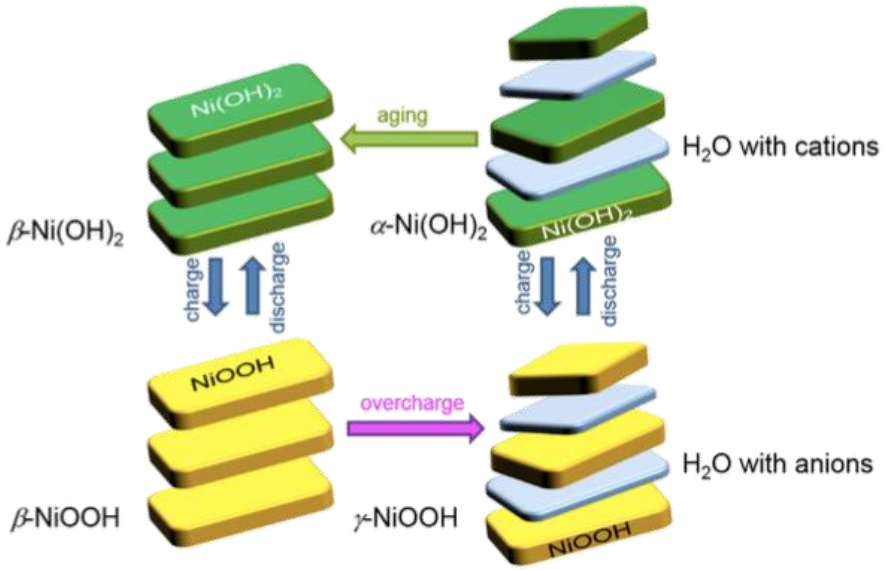
β-$Ni(OH)_2$



α-$Ni(OH)_2$



$Ni(OH)_2$ under charge/discharge



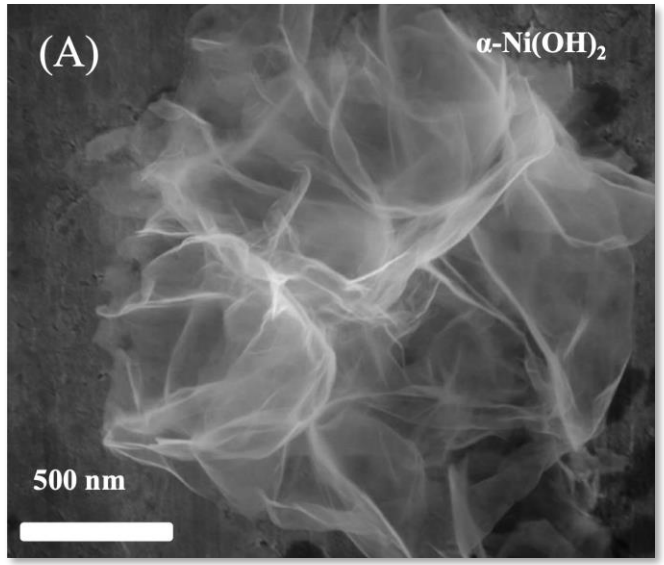
• Young, Wang, Yan, Liao, Meng, Shen, Mays, *Batteries* **3** (2017) 6

• Hall, Lockwood, Bock, MacDougall, *Proc. R. Soc. A* **471** (2015) 20140792

Objectives & Approach

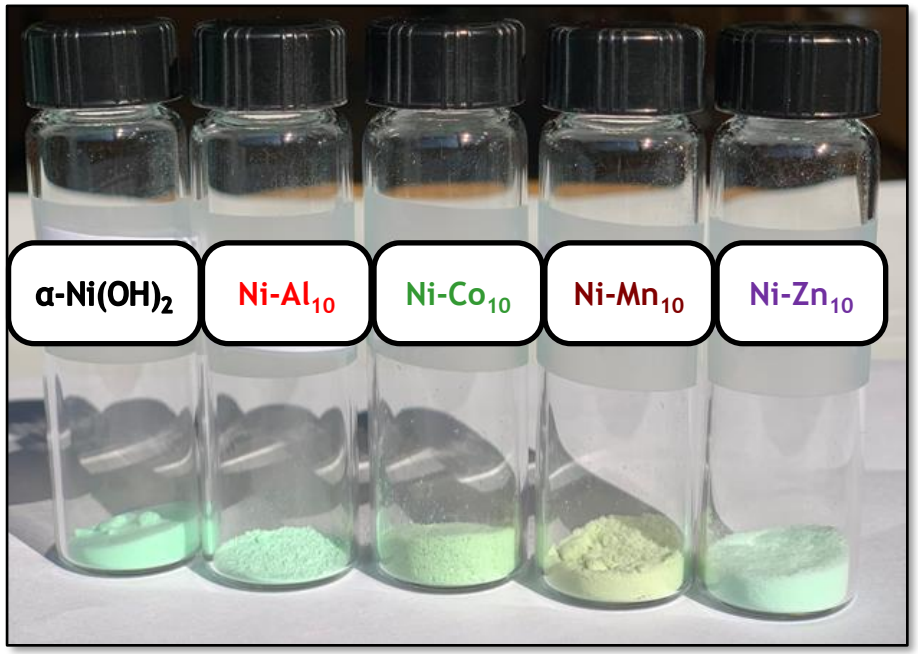
Objectives

- Determine the effects of metal substitution on the structure & electrochemical properties of microwave-synthesized α-$Ni(OH)_2$ nanosheets
- Evaluate metal substituent's ability to stabilize structure & enable higher capacity charge storage



Adapted microwave protocol

9:1 Ni to M substitution
(M = Al^{3+} , Co^{2+}, Mn^{2+}, Zn^{2+})



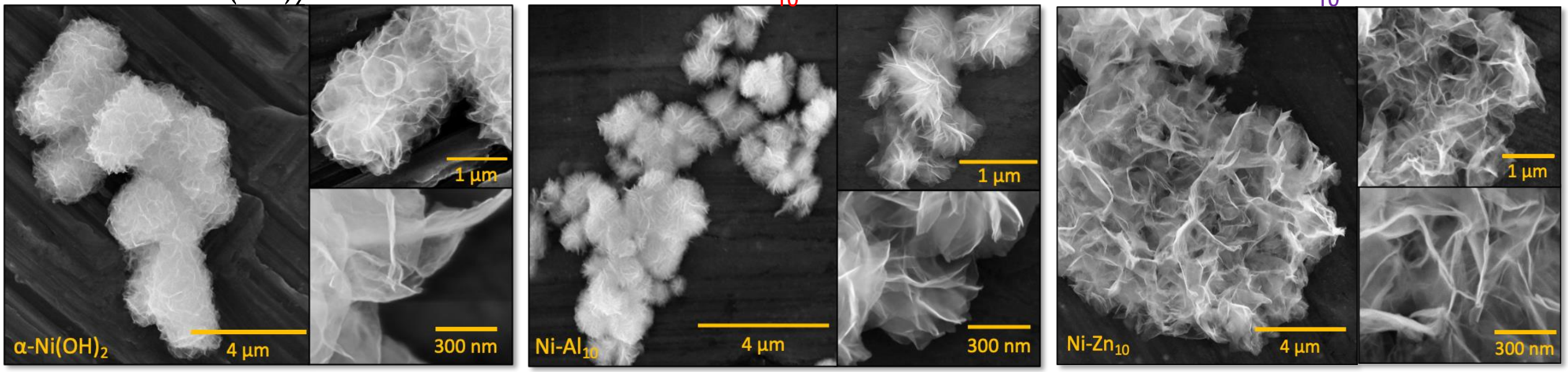
Approach

- Microwave synthesis of metal-substituted, α-$Ni_{0.90}M_{0.10}(OH)_2$, nanosheets
- Fabricate & cycle metal-substituted α-$Ni(OH)_2$ cathodes in alkaline Ni–Zn cells within Zn sponge anodes
  - Device-relevant mass loadings (≥10 mg · cm^{-2} active material)
  - Probe $Ni^{2+/3+}$ redox & oxygen evolution reaction (OER) onset

- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060
- Godínez-Salomón, Albiter, Alia, Pivovar, Camacho-Forero, Balbuena, Mendoza-Cruz, Arellano-Jimenez, Rhodes, *ACS Catal.* **8** (2018) 10498

Effects of Substitution on Morphology & Composition

α-$Ni(OH)_2$ | $Ni\text{-}Al_{10}$ | $Ni\text{-}Zn_{10}$

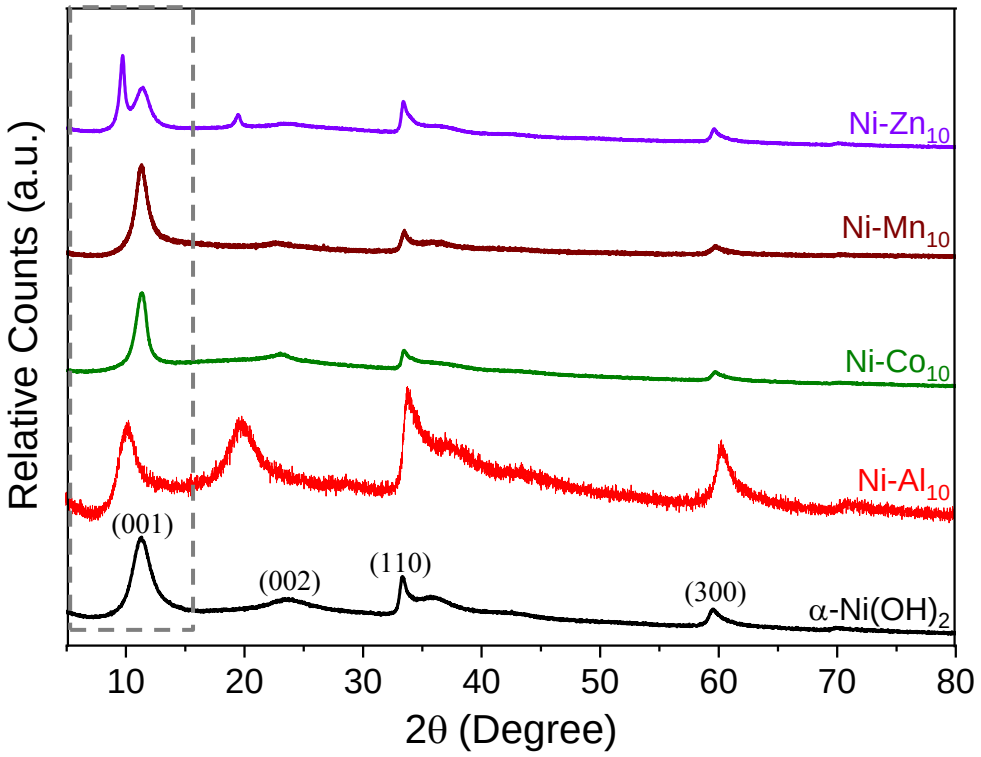


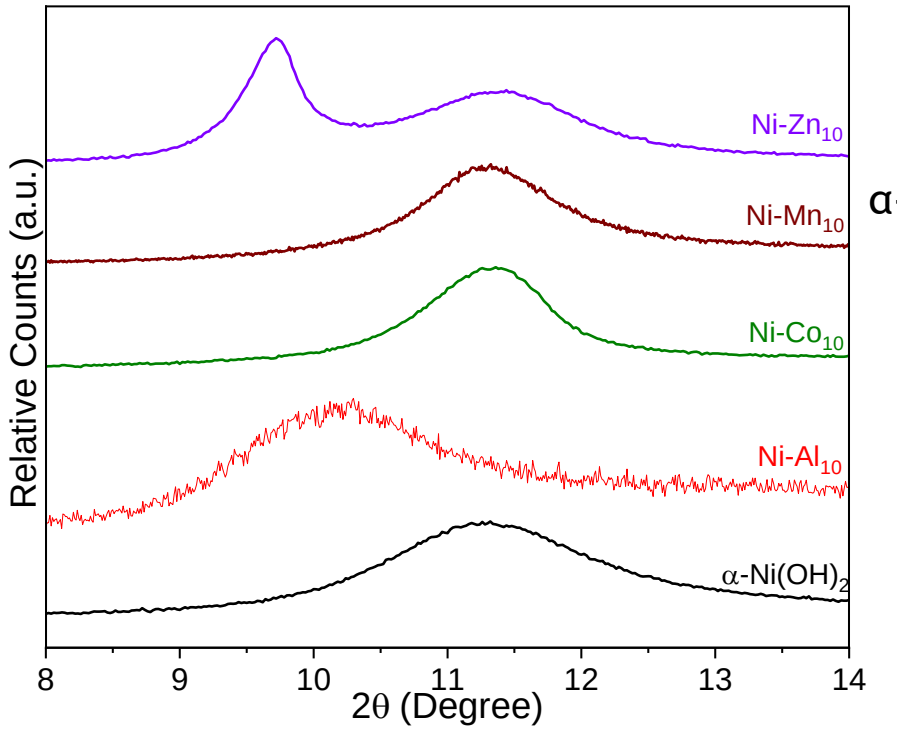
- Interconnected nanosheets (~2–12 nm thick) agglomerate into larger aggregates
- Maintained nanosheet morphology with substituents
- Substituent influences size of nanosheet aggregates
  - $Ni\text{-}Al_{10}$ → Smaller more densely packed nanosheets
  - $Ni\text{-}Zn_{10}$ → Larger nanosheet aggregation
- Uniform distribution of Ni & Al within structure
- Al^{3+} & Zn^{2+} > synthetic substitution ratio
- Co^{2+} substitution nominal to precursor stoichiometry
- Mn^{2+} << initial precursor stoichiometry

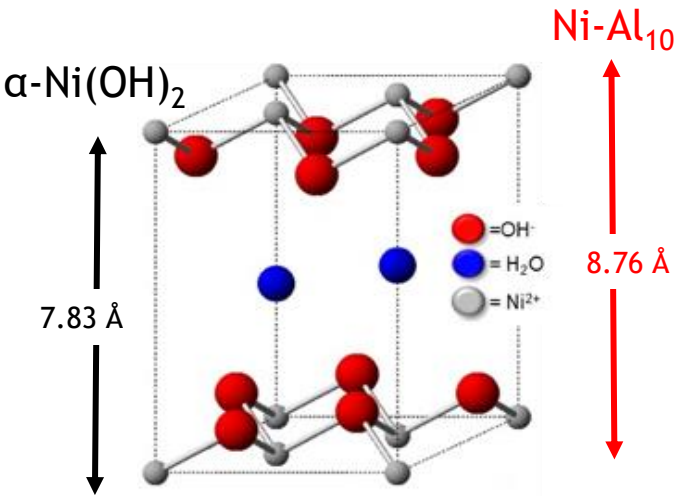
Relative atomic % from ICP analysis	
α-$Ni(OH)_2$	–
$Ni\text{-}Al_{10}$	$Ni_{0.87}Al_{0.13}$
$Ni\text{-}Co_{10}$	$Ni_{0.90}Co_{0.10}$
$Ni\text{-}Mn_{10}$	$Ni_{0.98}Mn_{0.02}$
$Ni\text{-}Zn_{10}$	$Ni_{0.84}Zn_{0.16}$

- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060

X-Ray Diffraction of Metal-substituted α-$Ni(OH)_2$





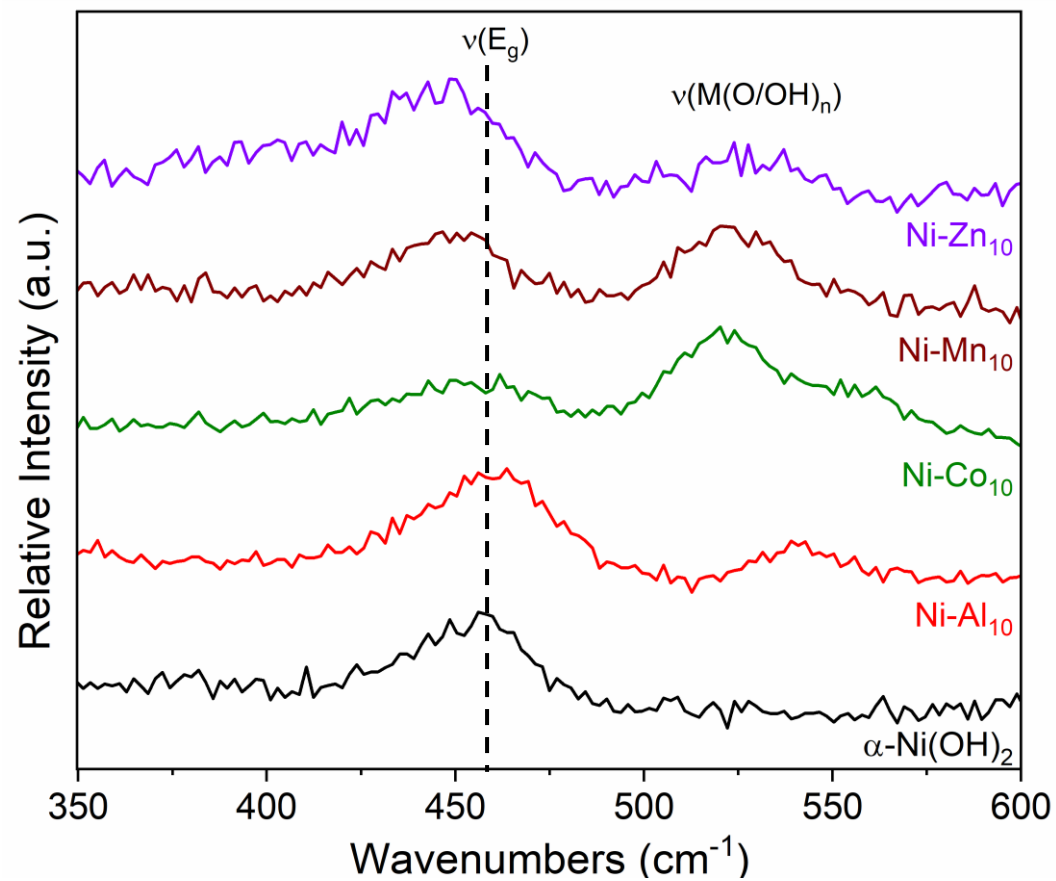


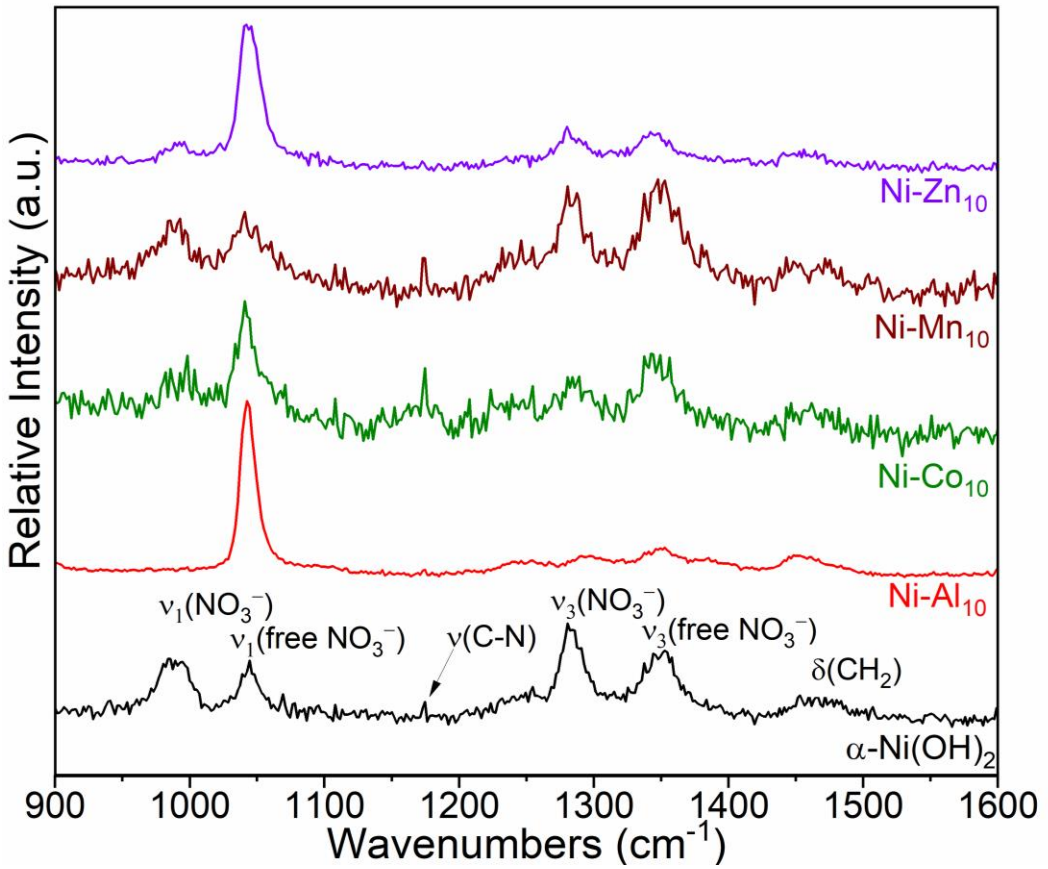
Retain layered α-$Ni(OH)_2$ crystal structure with substitution

- $Ni\text{-}Al_{10}$ → Increases interlayer spacing
- $Ni\text{-}Zn_{10}$ → Two-phases

- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060
- Hall, Lockwood, Bock, MacDougall, *Proc. R. Soc. A* **471** (2015) 20140792

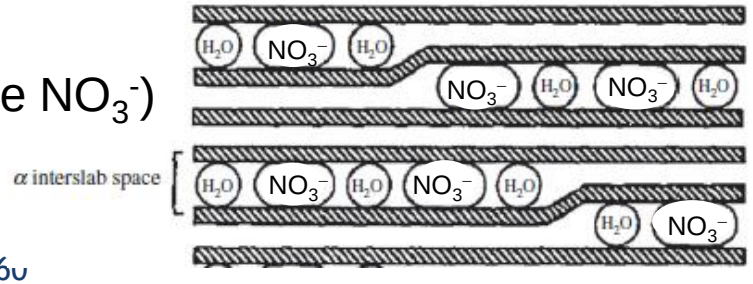
Raman Spectroscopy of Metal-substituted α-$Ni(OH)_2$





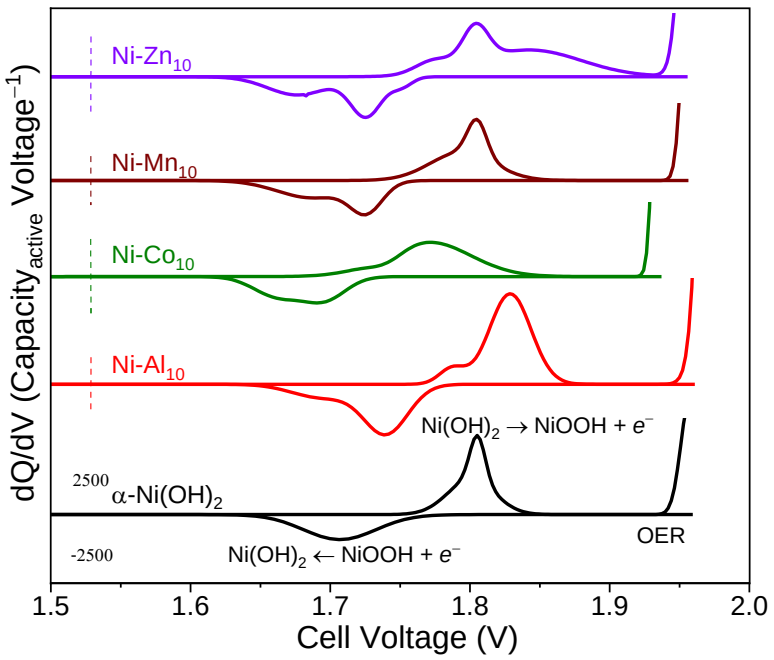
- Metal substitution induced changes in α-$Ni(OH)_2$ lattice modes
- Al^{3+} shortens Ni-O bond length
- New Raman bands indicates intra-lattice substitution

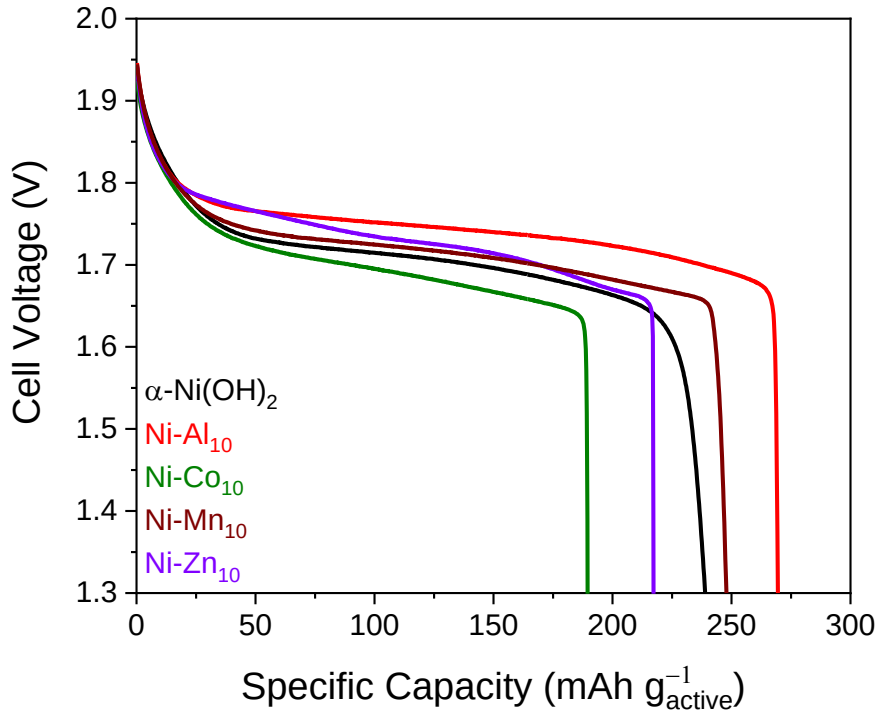
$Ni\text{-}Al_{10}$ →
Al^{3+} increases ν(free NO_3^-)

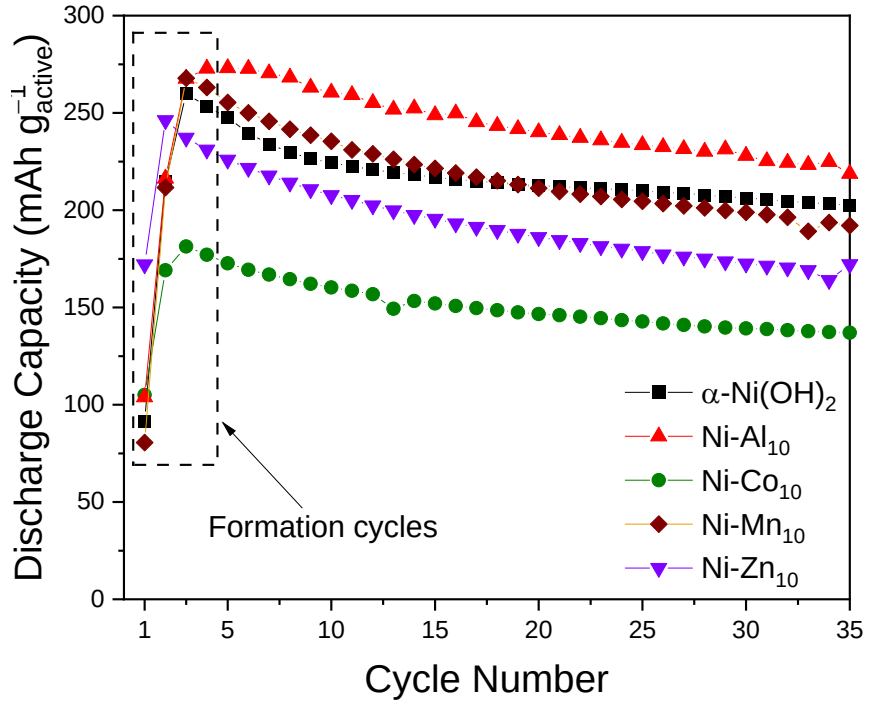


- Chen, Xiong, Zhao, Mahmoud, El-Sayed, Liu, *Adv. Sci.* **3** (2016) 1500433
- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 306υ

Galvanostatic Charge–Discharge of Metal-substituted α-$Ni(OH)_2$





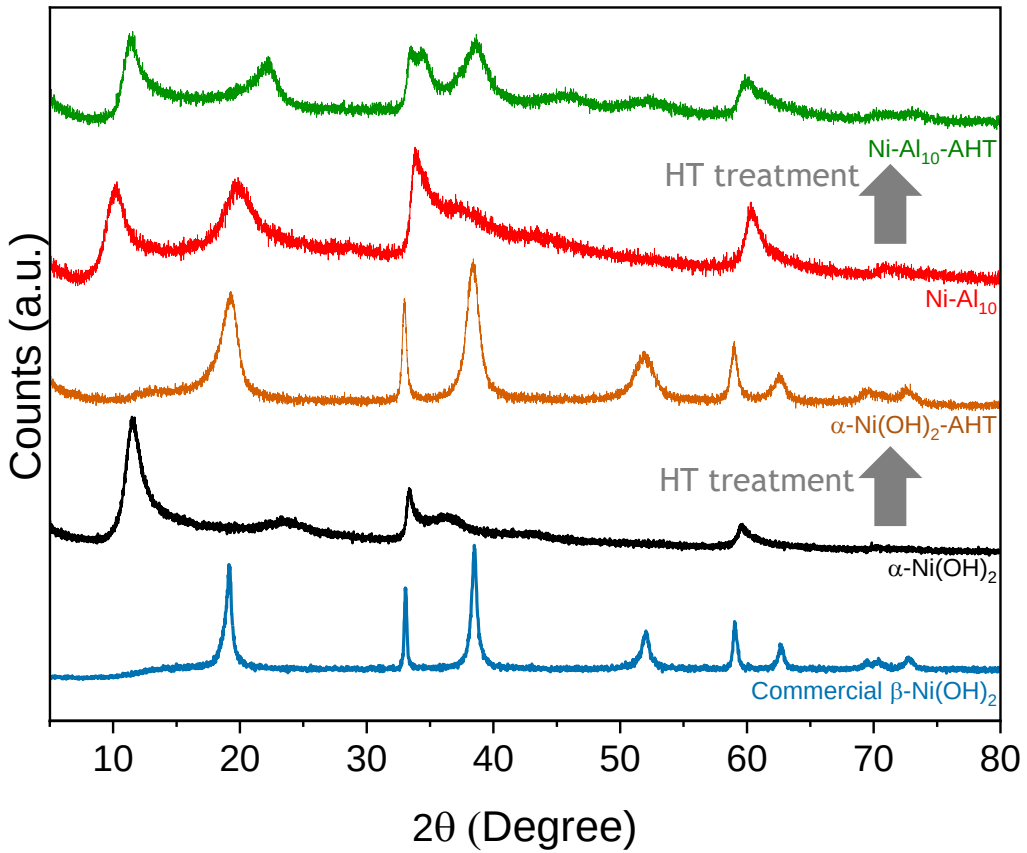


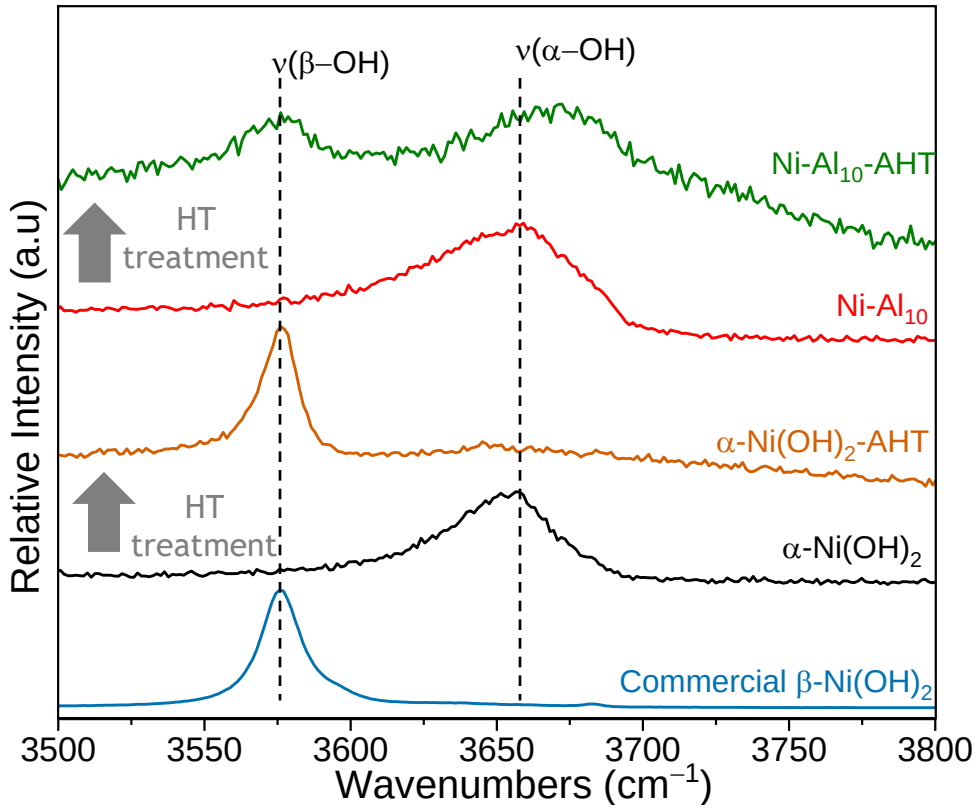
- Cathode performance evaluated using an intentionally aggressive charging protocol to determine OER onset (parasitic reaction)
- Substituents shift Ni redox & OER onset voltages
  - $Ni\text{-}Al_{10}$ → Increased OER onset
- Metal substituents influence cycling performance
  - $Ni\text{-}Al_{10}$ → Increased discharge capacity and voltage
  - Al^{3+}-substituted material maintained higher capacity upon cycling



- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060

Does Al^{3+} Stabilize the α-$Ni(OH)_2$ Phase?





- *Ex-situ* test of powders: Convert α-$Ni(OH)_2$ nanosheets to β-$Ni(OH)_2$ nanosheets in 0.01 M NaOH (180°C for 2 hrs)
- Improved alkaline-phase stability of α-$Ni(OH)_2$ with Al^{3+} substitution
  - Higher concentration of ordered free nitrate between the layers
  - Pillars the interlayer → *prevents β-$Ni(OH)_2$ formation*

- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060

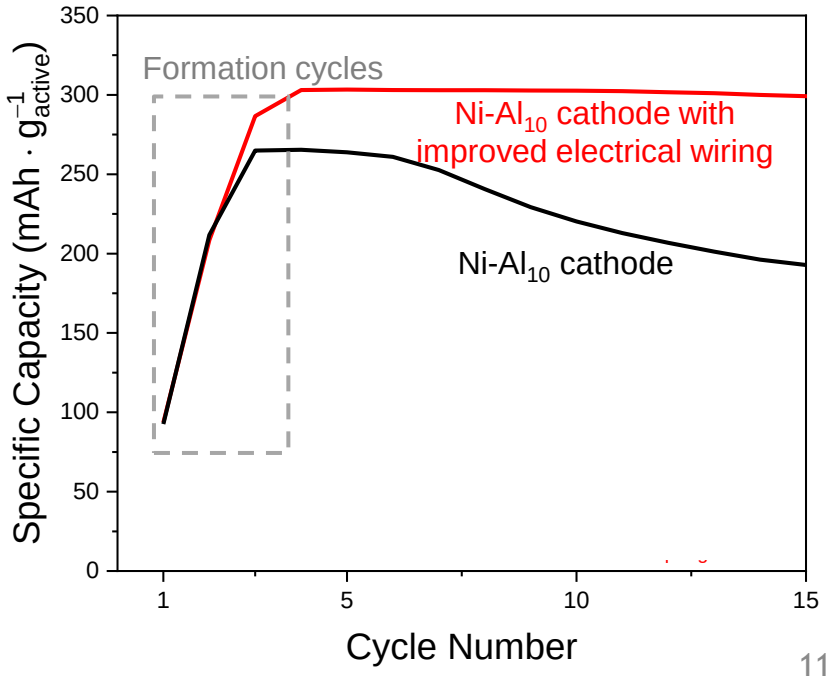
Conclusions & Next Steps

Conclusions

- Metal-ion substituents (Al, Co, Mn, Zn) influence structure, electrochemistry, and stability of microwave-synthesised α-$Ni(OH)_2$
- Al^{3+} substitution shortens Ni–O bond, orders interlayer anions $\Rightarrow$ increases discharge capacity, voltage and OER onset
- Important role of interlayer anions: provide necessary charge balance of Al^{3+} for Ni^{2+}
  - Stabilize the α-phase by preventing collapse of the layers
  - Lower the electrostatic burden at Ni sites
- Both effects enable extra electron charge to be stored & released

Next Steps

- Maintain high-capacity α-phase with cycling
  $\Rightarrow$ Improve electrical wiring within cathode volume
- Match charged state of Ni cathode to Zn anode
- Balance capacity of Ni cathode to Zn anode
- Evaluate rate capabilities



- Kimmel, Hopkins, Chervin, Skeele, Ko, DeBlock, Long, Parker, Hudak, Stroud, Rolison, Rhodes, *Mater. Adv.* **2** (2021) 3060

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