Advanced Cathodes for Intermediate-Temperature Na-Metal Halide Batteries

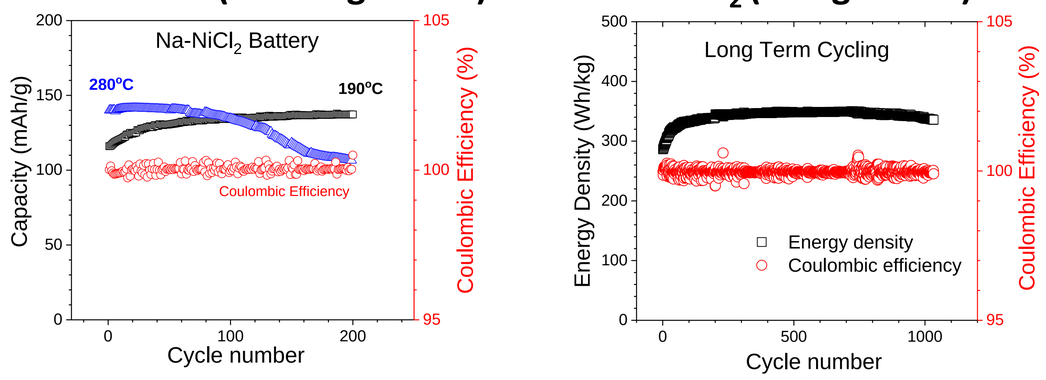
Xiaowen Zhan, Xiaochuan Lu, Jeff F. Bonnett, Nathan L. Canfield, David M. Reed, Vincent L. Sprenkle, and Guosheng Li*

Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

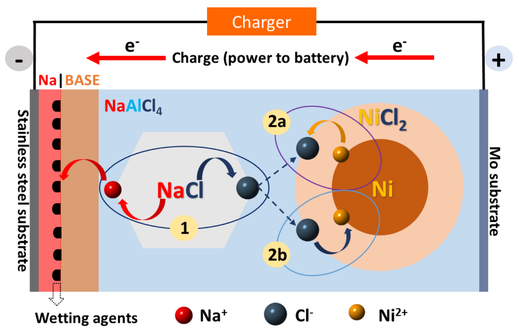
Background: IT Na-MH Battery Technology

2NaCl + Ni (discharge state) ↔ 2Na + $NiCl_2$ (charge state)



- Slow cell degradation (particle growth) and excellent cycling stability[1]
- Low-cost polymer sealing[2]

Challenge: Limited Rate Capability @ Lower T



PNNL solutions

- Anode Interface engineering
  - ➢ Bilayer BASE design[3]
  - ➢ Na/BASE wetting agents[4]

Objective: Determine the cathode reaction kinetics and further improve the rate performance.

From Ni/NaCl to Ni/NaX (Br and I) Cathodes[5]

Theoretical Reactions:

2NaCl + Ni ⇔ 2Na + $NiCl_2$

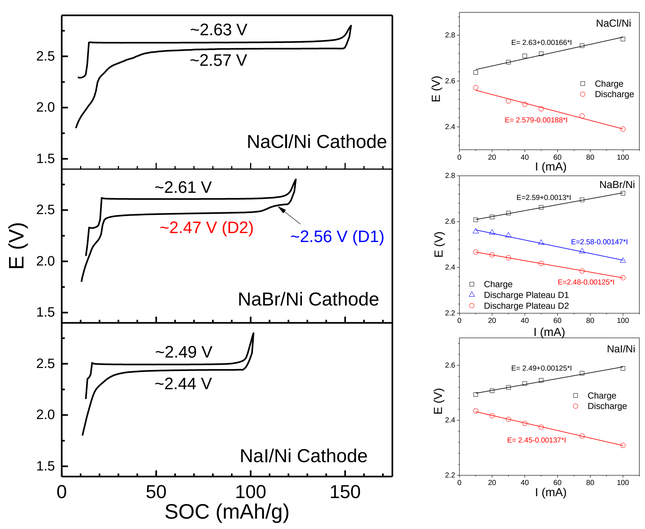
E_o = 2.60 V at 190°C

2NaBr + Ni ⇔ 2Na + $NiBr_2$??

E_o = 2.57 V at 190°C

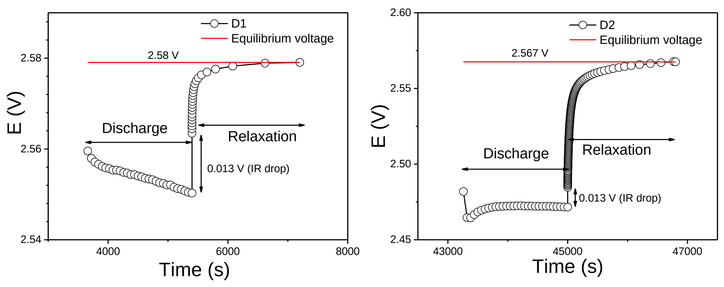
2NaI + Ni ⇔ 2Na + NiI_2

E_o = 2.46 V at 190°C



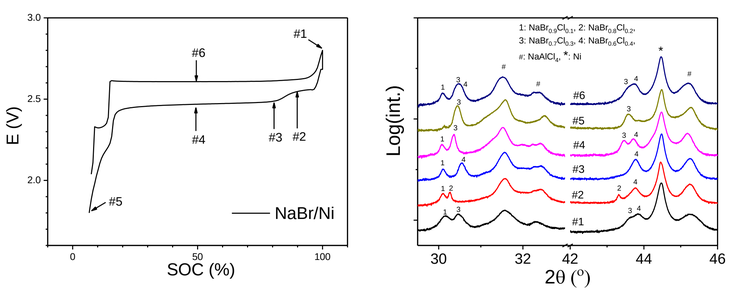
GITT:

- Same IR drop of 0.013 V (1.3 Ohm) for D1 and D2
- Extra overpotential for D2 possibly from mass diffusion

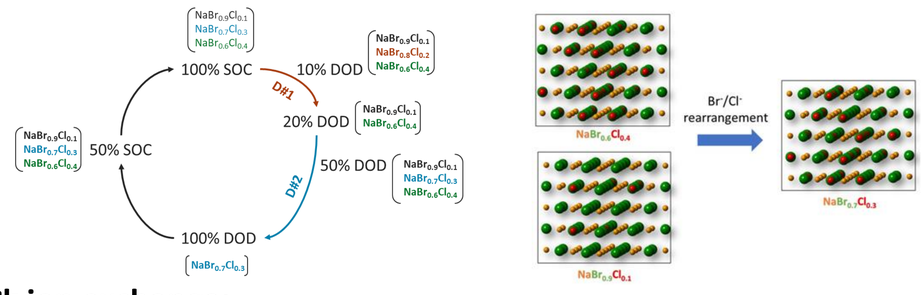


XRD & Synchrotron HR-XRD:

- Different $NaBr_xCl_{1-x}$ mixed phases identified
- $NiBr_{2x}Cl_{2-2x}$ rather than $NiBr_2$ forms during charge



Origin of Extra Discharge Plateau



Br^-/Cl^- ion exchange:

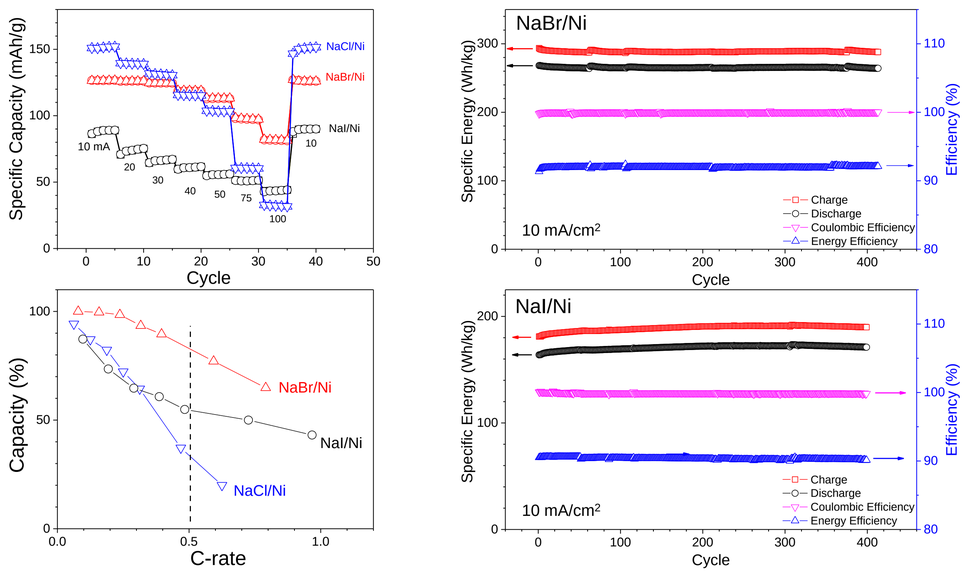
$xNaBr + NaAlCl_4 \Leftrightarrow xNaCl + NaAlBr_xCl_{4-x}$

- Confirmed by LC-Mass result: x=0.24

Overall cell reaction:

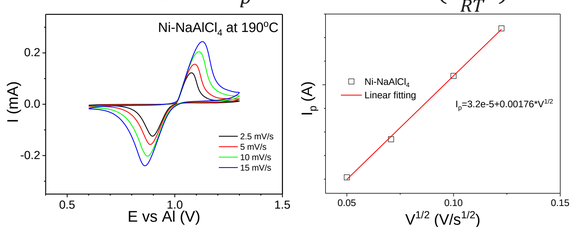
$2NaBr_xCl_{1-x} + Ni \Leftrightarrow 2Na + NiBr_{2x}Cl_{2-2x}$ (E_o = 2.58 V)

Superior Rate Performance of NaBr/Ni



Fast Salt Dissolution → Rate Enhancement

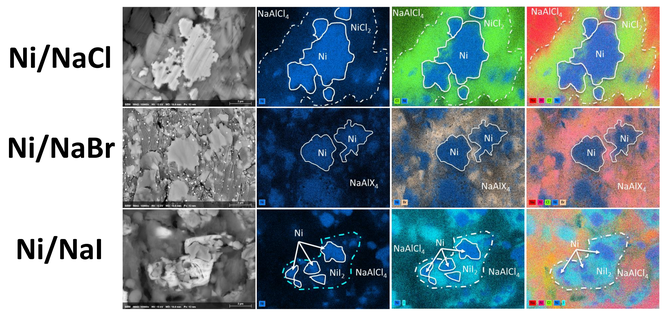
Randles-Sevcik: $i_p = 0.4463nFAC(\frac{nFvD}{RT})^{1/2}$



Diffusivity from CV

Cathode	D (cm^2/s)
$NiCl_2$	1.9×10^{-8}
$NiBr_2$	**1.0×10^{-8}**
NiI_2	3.0×10^{-8}

Slower diffusion: thin $NiBr_2$ layer



Solubility from ICP

Sample	Solubility
NaCl	2.2 mol%
NaBr	**6.6 mol%**
NaI	2.4 mol%

Faster salt dissolution (rate-determining step): high rate capability

Conclusions:

- **The NaBr/Ni cathode delivered 174 Wh/kg at 100 mA (~0.8C), which is 2.5 times of conventional NaCl/Ni cells.**
- **The superior rate capability of NaBr/Ni is ultimately attributed to the faster sodium bromide salt dissolution, which enables easier Br^- anion transfer.**

Acknowledgments

This work is supported by U.S. Department of Energy (DOE) Office of Electricity (Contract No. 70247) and partially by the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning, the Republic of Korea Ministry of Trade, Industry & Energy (No. 20158510050010) and POSCO. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. PNNL is operated by Battelle for the DOE under Contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

Contact: Guosheng Li, Ph.D.
Battery Materials & Systems Group
Pacific Northwest National Laboratory
Email: guosheng.li@pnnl.gov

[1] Li et al., *Nat. Commun.* 7, 10683 (2016).
[2] Change et al., *J. Power Sources*, 348, 150 (2017).
[3] Jung et al., *J. Power Sources*, 396, 297 (2018).
[4] Chang et al., *J. Mater. Chem. A*, 6, 19703 (2018).
[5] For more details of this work please refer to: Zhan et al., **Elucidating the role of anionic chemistry towards high-rate intermediate-temperature Na-metal halide batteries**, *Energy Storage Maters.*, https://doi.org/10.1016/j.ensm.2019.08.021.