Mitigating Capacity Loss of Copper Oxide Cathodes in Rechargeable Batteries

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Abstract

Developing safe and cost-effective batteries will improve energy storage and capacity for intermittent energy sources. Alkaline Zn-CuO batteries are promising candidates for improving safety and reducing cost. These batteries have a high theoretical capacity and are based on earth-abundant, inexpensive materials. Importantly, it is compatible with aqueous electrolytes, which are non-flammable and offer higher ionic conductivities. However, CuO cathodes were found to have active material dissolution and migration from the electrode into the separator. So, we began to study how to mitigate this dissolution and migration during cycling. In terms of altering electrolytic concentration, the 25% KOH had lower capacity loss compared to 35%, with both showing better results than the 15% KOH, and supporting electrolyte was beneficial to battery capacity. The addition of a graphite layer, however, was not beneficial to the battery, showing similar or worse capacity degradation. Finally, we used a rotating ring-disk electrode (RRDE) to analyze when the dissolved species appears, and learned that it appears during the charge process.

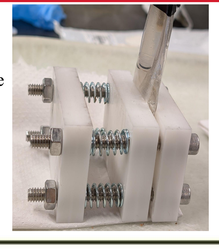
Background

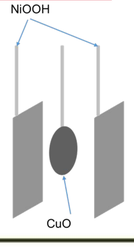
- The need for effective energy storage systems is increasingly critical as wind and solar energy are becoming more prominent.
- Lithium-based batteries are widely used but are expensive and pose a fire hazard
  - CuO-Zn-based batteries are inexpensive, readily available, and compatible with aqueous electrolyte
- The addition of bismuth oxide in the copper oxide cathode has allowed for reversibility of its reaction
  - Bismuth oxide decreases cell resistance and promotes reduction of copper
- Maintaining the capacity throughout cycling is challenging due to the dissolution of copper to the separator inside the cell
  - This forms cuprous oxide (Cu_2O)
    - To address the copper loss, we tested electrolyte concentration and added an interlayer of graphite surrounding the cathode

Cell Fabrication

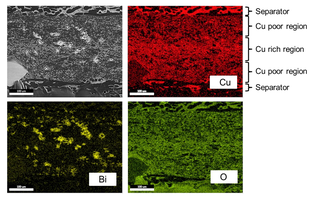
55% CuO cathode pressed on a nickel mesh current collector, wrapped in a Freudenberg separator, and sandwiched between NiOOH anodes and layers of separators; all placed in a pouch with electrolyte, and compressed

(Left): cell in compression
(Right): simple diagram of battery cell



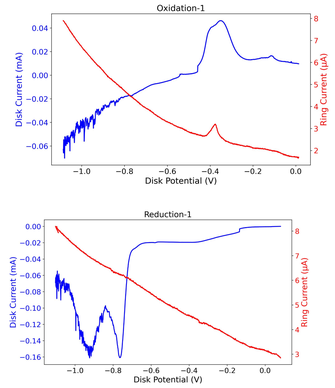


Dissolution/ RRDE



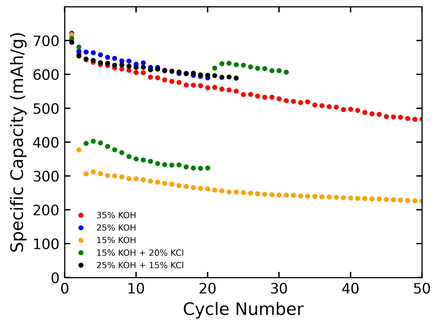
- Noticed a decrease in copper material in the cathode throughout the charge process and an increase of it in separator
- $Cu(OH)_2 + 2OH^- \rightarrow [Cu(OH)_4]^{2-}$

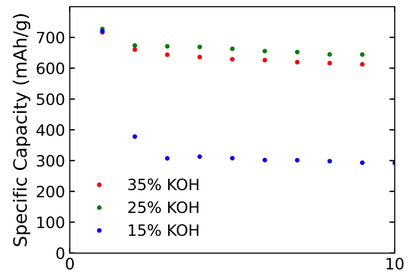
- No soluble species formation during discharge process
- During oxidation, ring current peak was observed even though the ring was held at oxidizing potential compared to the disk.



Alteration of Electrolyte

- Altered the electrolyte concentration in the battery cell to:
  - Rid of any excess OH^- ions in the cell
  - Prevent/slow creation of $[Cu(OH)_4]^{2-}$
- Prepared 3 similar cells with 35% KOH, 25% KOH, and 15% KOH
- 25% KOH and 35% KOH showed similar, strong results, while 15% KOH capacity decreases quickly





- Added a supporting electrolyte to ensure efficient ion transport while decreasing the OH^- concentration
- Made 2 cells connected to reference electrodes in order to pull data specifically from the cathode (capacity, voltage, etc.)
  - 25% KOH, 10% KCl
  - 15% KOH, 20% KCl
- Supporting electrolyte seems beneficial to battery capacity

Graphite Layer

- Tested interlayer of graphite between cathode and separator to:
  - Act as a physical barrier to trap migrating Cu_2O particles & reduce material loss to the separator.
- Two cells were prepared in 35% KOH:
  - One with a 20 mg graphite layer on each side of the cathode.
  - Another with a 40 mg graphite layer on each side.

Cell with 20 mg graphite during cycling

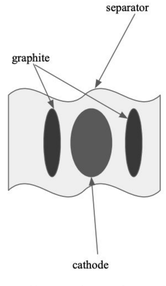
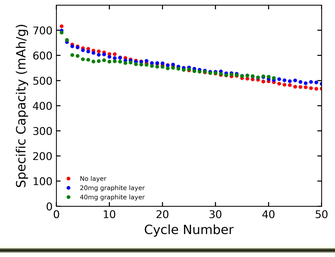
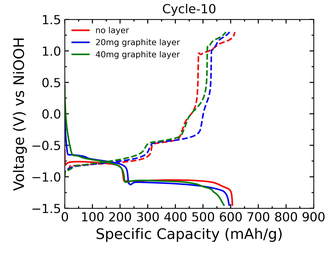


Illustration of graphite layer

- The 20 mg and 40 mg graphite layers showed similar capacity loss to a control cell without the interlayer





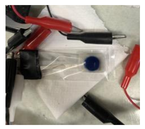
Conclusion

- Cannot block the cathode from the electrolyte → prevents efficient ion transfer
- Balanced amount of OH- ions

Future methods of improving experimental design…

- Improving/changing separators to reduce porosity while still allowing ion transfer
- Add Cu_2O to electrolyte to form $[Cu(OH)_4]^{2-}$
  - Saturation point is reached and no more dissolved species can be formed

(Left): cell with Cu_2O electrolyte
(Right): cathode after multiple cycles



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