Low-Cost Zinc-Ion Battery with Carbothermally Modified MnO_2 Cathode

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Abstract: We present a cost-effective Zn-ion battery cathode based on carbothermally treated MnO_2, where commercial EMD is coated with sucrose and mildly calcined to transform its mixed ε+R phases into a ε+β composition. This simple surface modification improves electrochemical performance with high Coulombic efficiency and a discharge capacity of ~92 mAh g^{-1}. The cathode exhibits excellent compatibility with both sulfate- and acetate-based aqueous electrolytes.

🔷 **Project Goal:** Develop a low-cost and scalable cathode strategy for aqueous ZIBs.

🔷 **Current Practice:** Commercial MnO_2 (EMD) typically exhibits poor cycling stability due to structural instability, Mn dissolution, and the presence of non-conductive R-phase. Additionally, most Zn-ion batteries rely on sulfate-based electrolytes, which can form passivating layers and limit long-term performance.

🔷 **Why This Matters:** The carbothermal method (sucrose + heat) promotes formation of stable ε + β polymorphs and introduces a conductive carbon network. The resulting cathode delivers >90 mAh/g capacity with excellent Coulombic efficiency and remains functional even in acetate-based electrolytes.

🔷 **Innovation:** Unlike prior work, this study demonstrates that simple surface engineering can achieve high reversibility and Zn storage performance, including under acetate electrolytes that lack Zn^{2+} in the starting formulation.

🔷 **Impact:** The process enables safer, long-lasting ZIBs using low-cost materials and mild processing, with potential for application in grid-scale energy storage.

🔷 **Alignment:** The approach aligns with DOE by utilizing abundant, non-toxic materials and eliminating the need for complex synthesis routes—supporting robust, affordable energy storage solutions.

MnO_2 Cathodes

Why MnO_2?

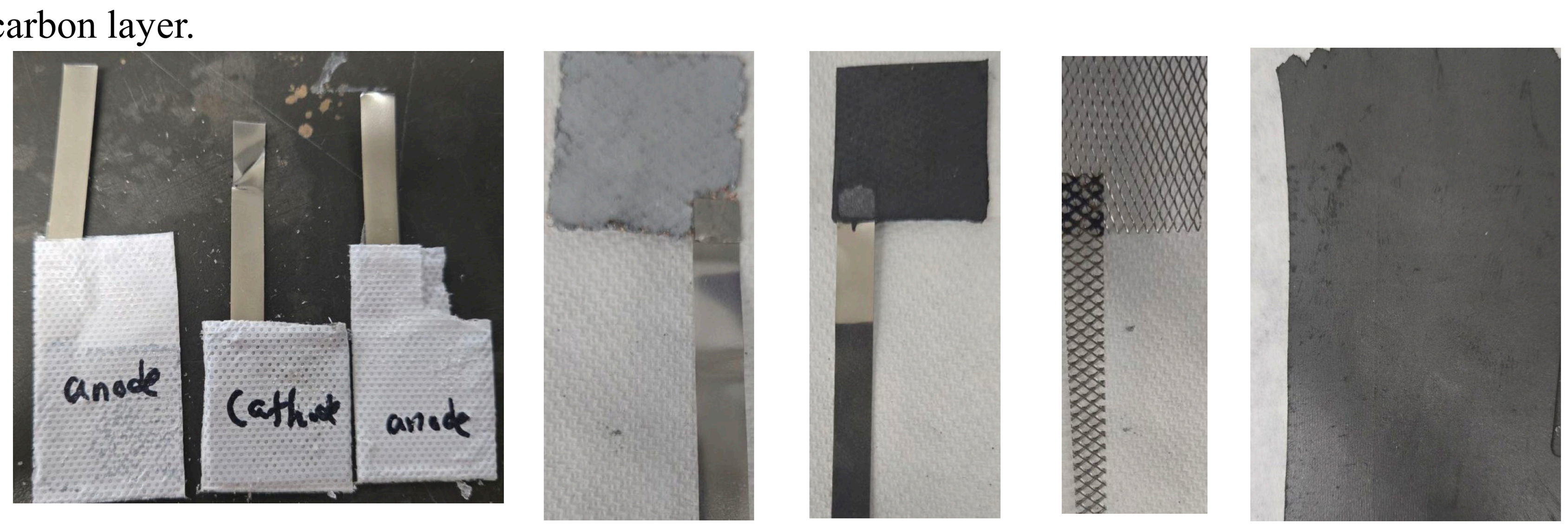
- Manganese dioxide is a low-cost & high-capacity cathode
- Pristine MnO_2 suffers from poor conductivity and gradual Mn^{2+} dissolution during cycling
- Strategies like metal doping and nanostructuring improve performance, they add complexity and cost
- A key issue is Mn loss in mildly acidic $ZnSO_4$ electrolytes, mitigated by adding Mn^{2+} salts

Our Approach – Carbothermal Modification

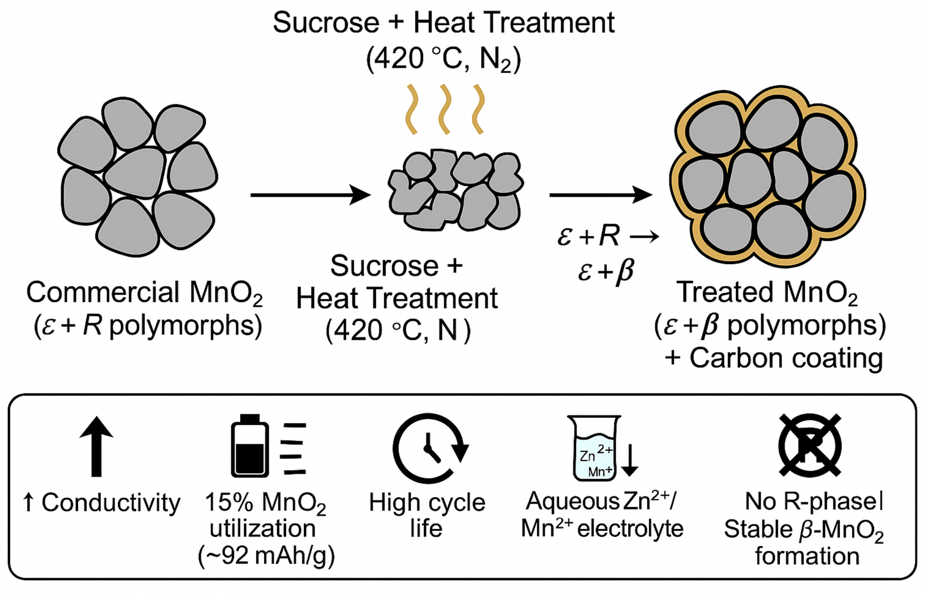
- A simple, low-temperature carbothermal treatment to modify commercial MnO_2 (EMD)
- Sucrose coating followed by calcination under inert gas
- Forms a carbon-rich surface and converts the ε + R polymorphs into a ε + β structure
- The carbon layer boosts conductivity, improving cycle life
- Unlike doping or hydrothermal methods, this process is scalable, low-cost, and industry-friendly

Methods

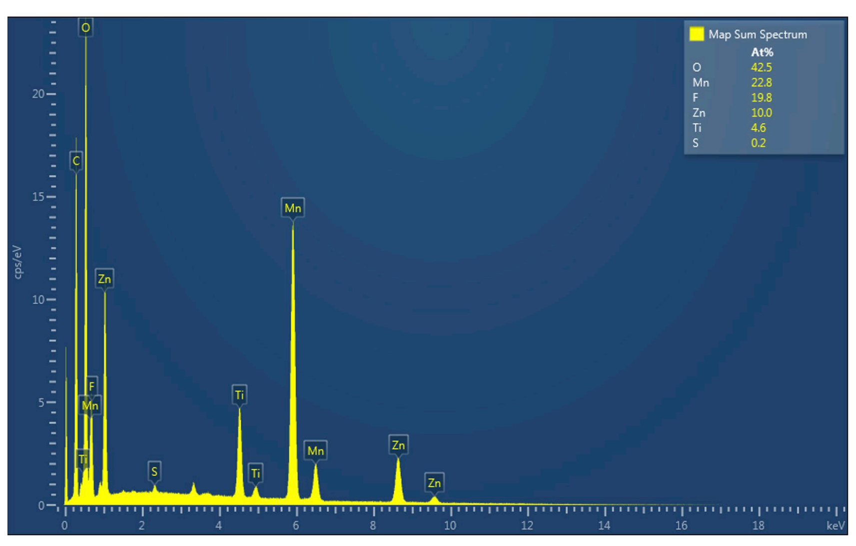
Carbothermal MnO_2 Synthesis:
EMD was coated with 0.5–3 wt% sucrose (in 20% ethanol–water), dried at 80 °C, and calcined at 420 °C in N_2. This treatment induced ε + R → ε + β phase transformation and formed a conductive carbon layer.



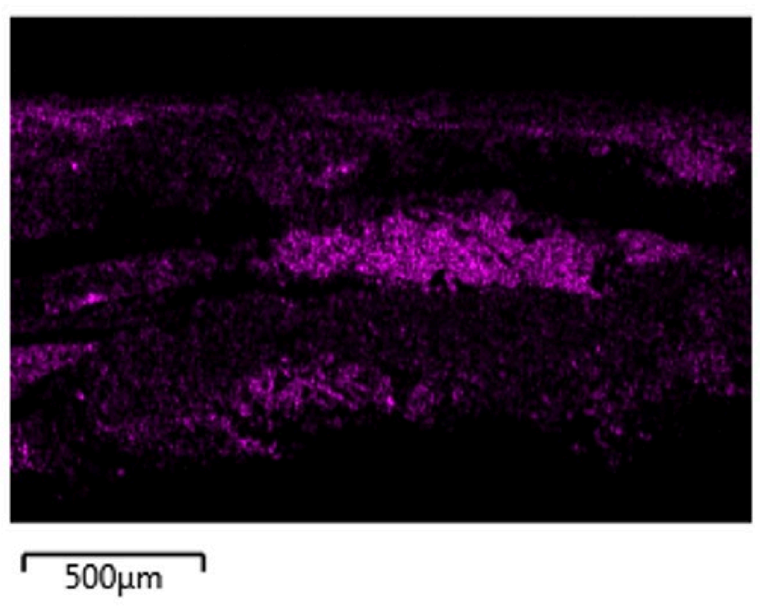
Mechanism



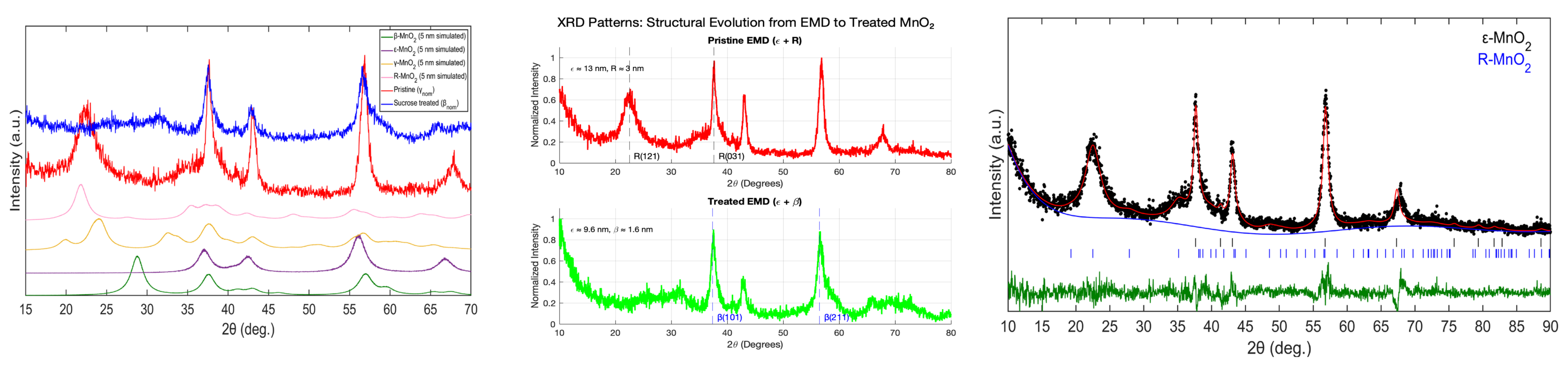
- Cross-sectional SEM–EDX mapping reveals Zn distribution within the cathode in K-acetate (Zn-free electrolyte)
- Zn signal detected in cathode after cycling Suggests Zn migration from anode into cathode
- Indicates Zn uptake by treated MnO_2 even without Zn^{2+} in electrolyte
- Possible Zn insertion
- **~10 at% Zn** detected in cycled MnO_2 electrode



Zn



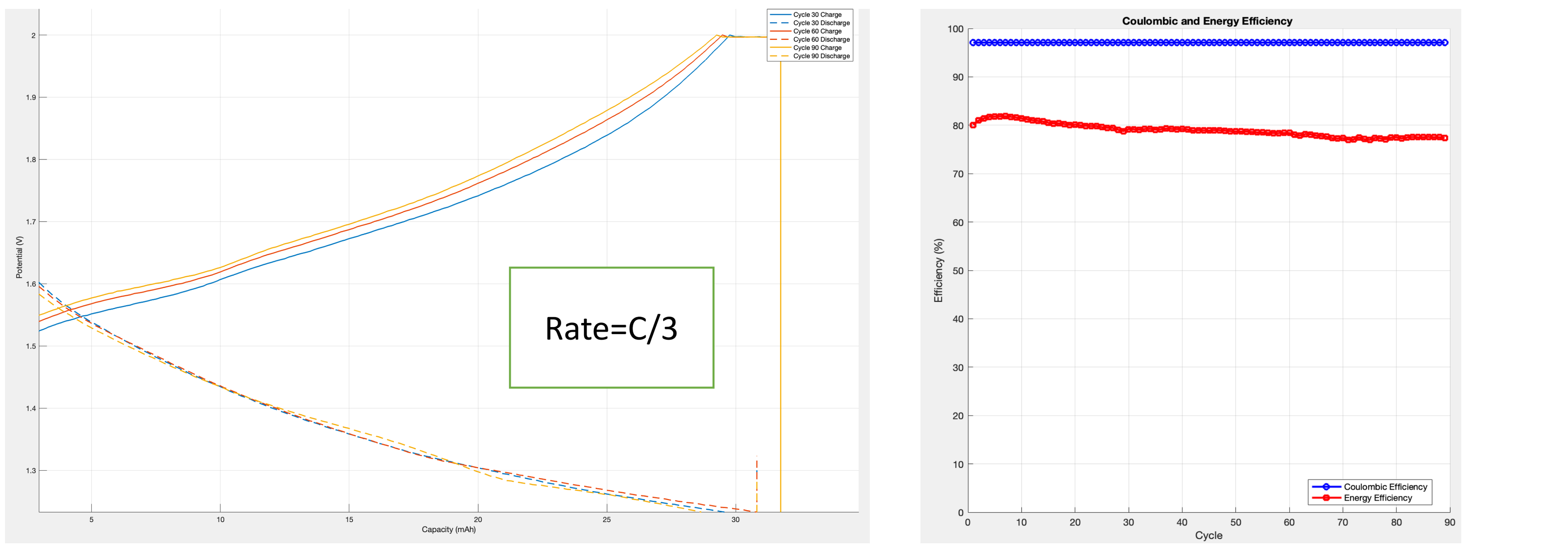
Results



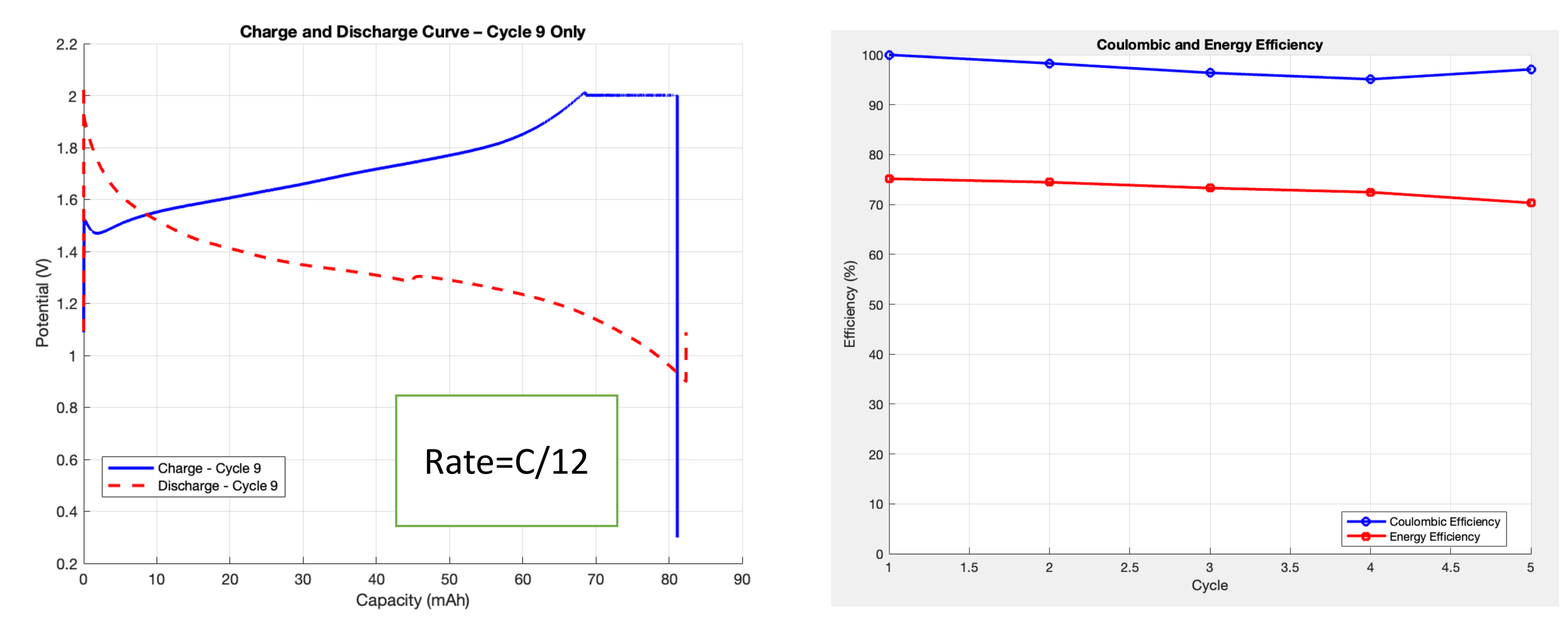
XRD confirmed that carbothermal treatment altered the MnO_2 structure.
After sucrose treatment, the **β-MnO_2 (pyrolusite) phase emerges (~23 wt%)** while the R-phase disappears.

XRD ➔ a structural shift from ε + R to ε + β MnO_2 after sucrose-assisted carbothermal treatment
Pristine EMD shows ε- and R-phase peaks (~22.5°, 37.66°)
Treated MnO_2 shows disappearance of R-phase and emergence of β-MnO_2 peaks (~37.4°, 56.5°)

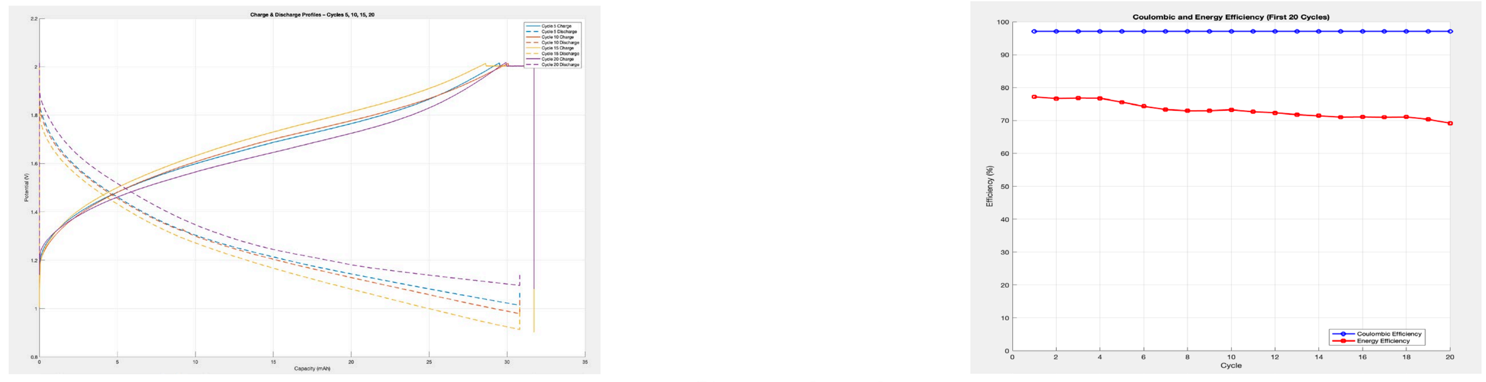
Long-Term Cycling Behavior at a Utilization Level of 31 mAh g^{-1}



Long-Term Cycling Behavior at a Utilization Level of 90mAh g^{-1}



Acetate-Based Electrolyte Compatibility



Conclusion

- Our low-cost carbothermal modification proves to be an effective strategy to improve ZIBs cathodes
- By coating MnO_2 with a carbon precursor and heating, we induced a favorable ε+β phase composition
- The treated MnO_2 shows significantly improved cycle life
- Can sustain deeper discharges
- It offers a practical path toward cheap, durable aqueous batteries

Future Work

- Increase Utilization: Optimize electrode and electrolyte to achieve beyond 92mAh/g
- Polymorph & Additive Integration: Explore other MnO_2 polymorphs or hybrid cathode compositions
- Scale-Up and Long-Term Testing
- Mechanistic Understanding: Investigate Zn^{2+} intercalation and phase changes in treated MnO_2

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