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Title Sodium Borohydride-Induced Surface Modification of Manganese Oxides for Optimized ORR Active Electrocatalyst

Jithul KP, Naina Sharma, Jay Pandey*

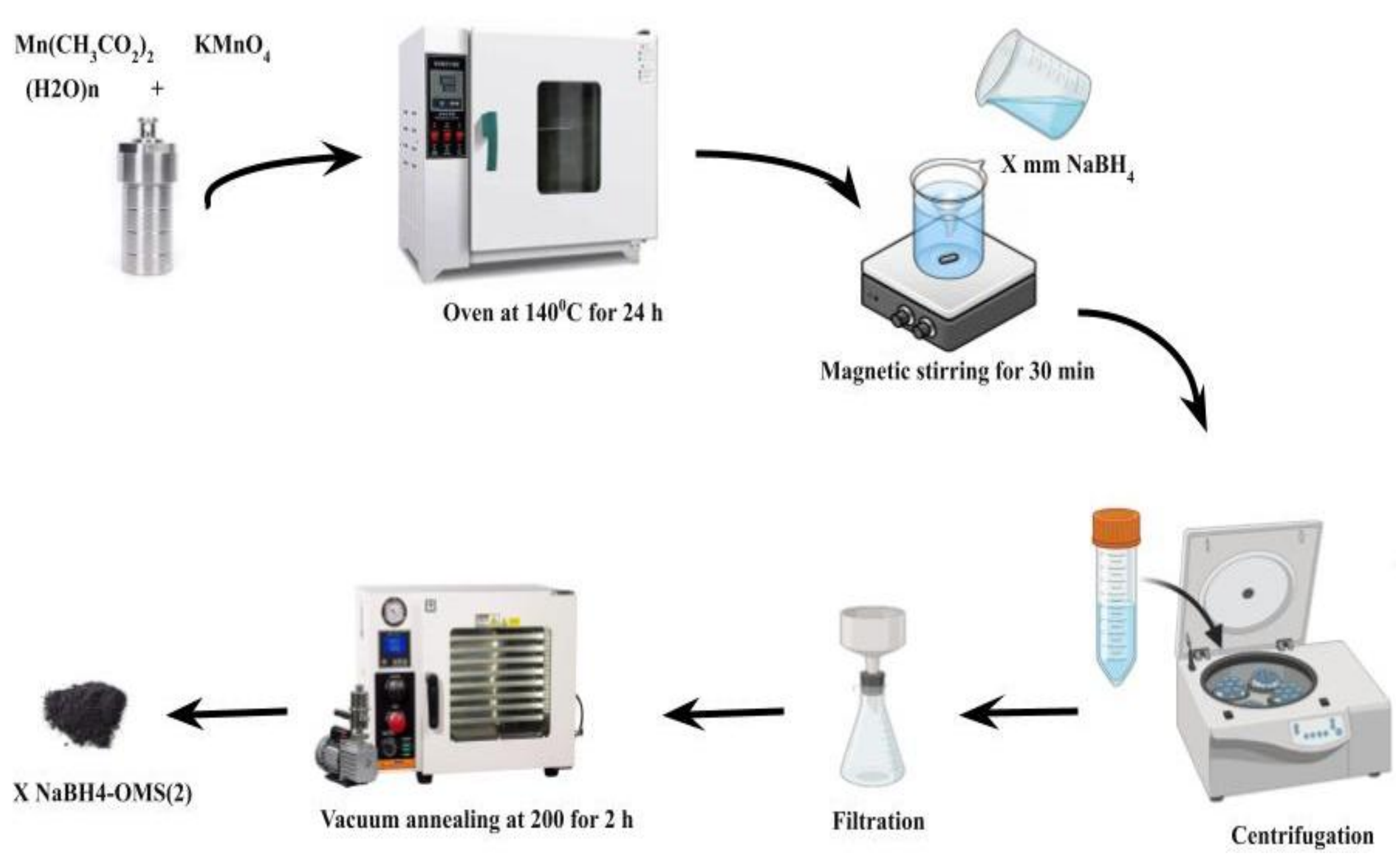
Department of Chemical Engineering, Birla Institute of Technology & Science Pilani, Pilani Jhunjhunu-333031, Rajasthan, India

INTRODUCTION & AIM

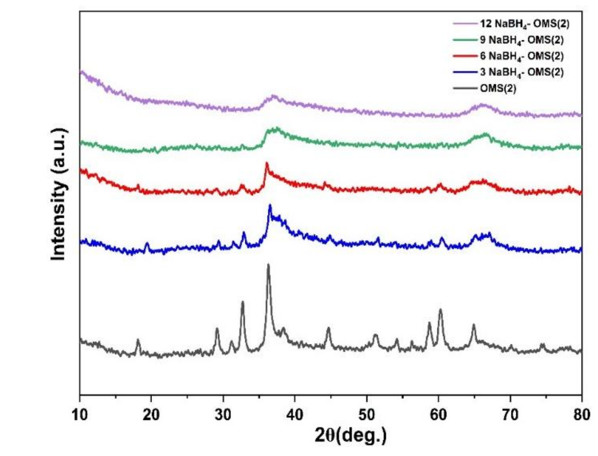
- The oxygen reduction reaction (ORR) is fundamentally important for clean energy conversion and storage technologies, offering a sustainable pathway.
- While platinum-based catalysts exhibit excellent ORR activity, their high cost and limited availability hinder widespread practical application.
- Manganese oxide octahedral molecular sieves (OMS(2)) are promising ORR catalysts due to cost-effectiveness and durability. However, low conductivity and activity limit their use.
- To optimize the oxygen vacancy concentration on the surface of OMS through a simple and scalable surface reduction etching treatment using sodium borohydride ($NaBH_4$).
- To investigate the effect of $NaBH_4$ treatment on the Mn^{3+}/Mn^{4+} ratio on the OMS surface and its correlation with ORR performance.
- To demonstrate the improved ORR performance of the optimized OMS material, showcasing its potential as a cost-effective alternative to traditional platinum-based catalysts.

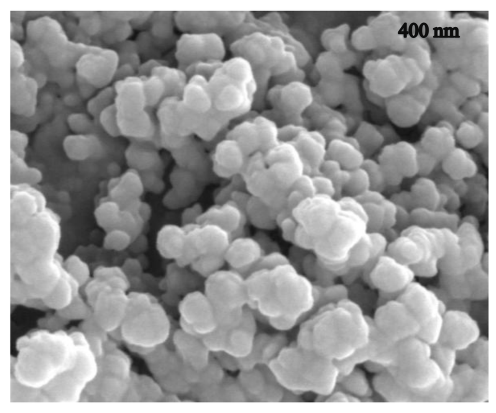
METHOD

Synthesis of $NaBH_4$-OMS(2) :

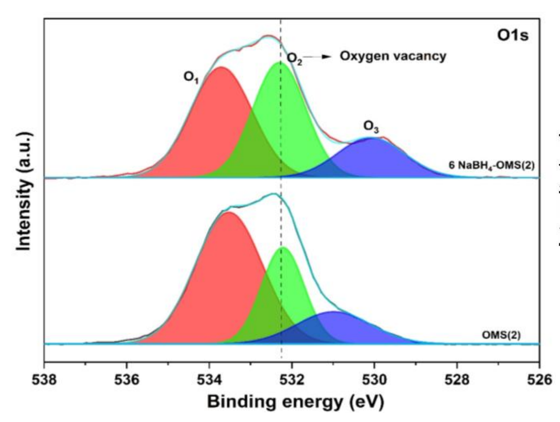


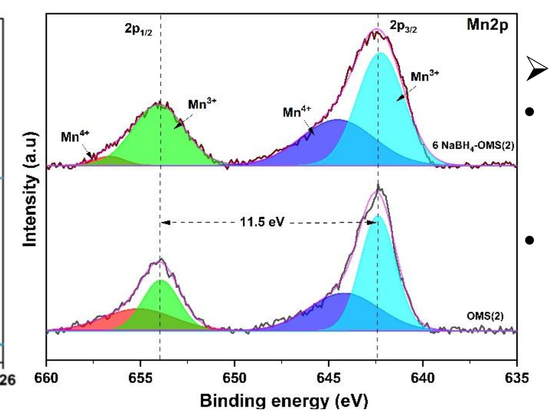
RESULTS & DISCUSSION



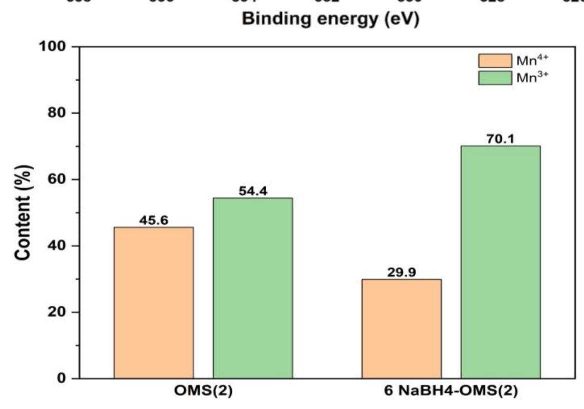


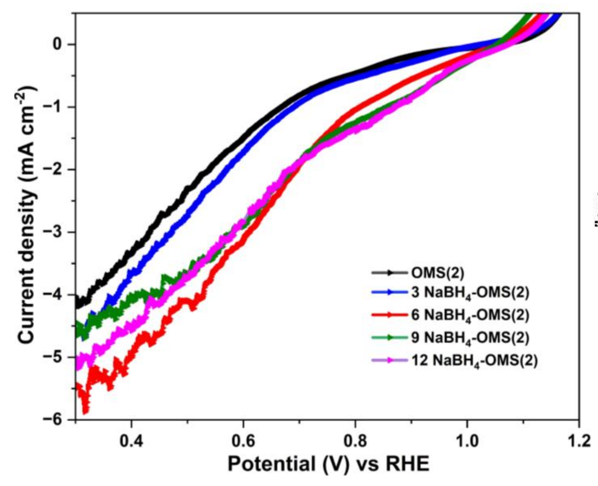
- **XRD :**
  - Increasing $NaBH_4$ concentration led to decreased XRD peak intensity, indicating reduced crystallinity.
- **FESEM :**
  - $NaBH_4$ treatment of OMS(2) exhibited nanospheres with an average diameter of 80.3 nm and resulted in a slightly more exposed surface.

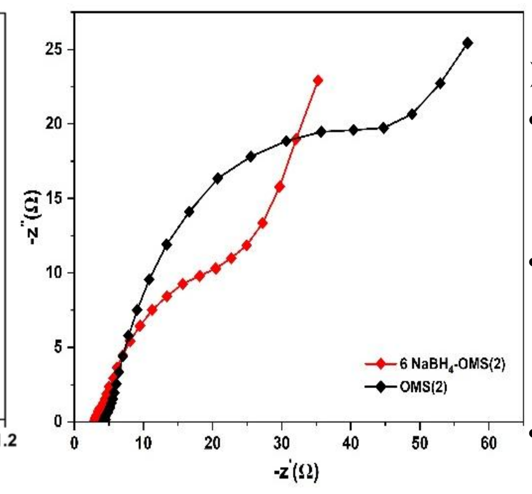


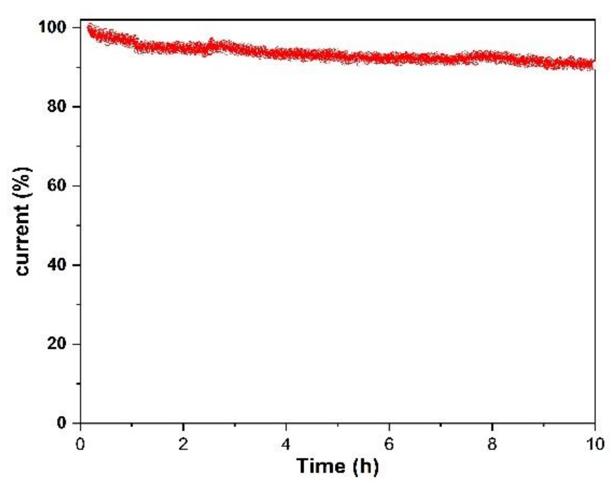


- **XPS :**
  - $NaBH_4$ treatment significantly increased the concentration of oxygen vacancies in the OMS(2) sample.
  - $NaBH_4$ treatment increased the relative Mn^{3+} content from 54.4% to 70.1% and decreased the Mn^{4+} content from 45.6% to 29.9%.









- **Electrochemical :**
  - The optimised OMS material exhibited a remarkable half-wave potential of 0.661 V.
  - EIS indicated that increased oxygen vacancies lower the low-frequency impedance and enhance ORR activity.
  - The catalyst maintained 90% of its initial current density after 10 hours, demonstrating exceptional stability for long-term electrochemical applications

CONCLUSION

- $NaBH_4$ treatment enhances OMS-2 ORR activity via oxygen vacancies and optimize Mn^{3+}/Mn^{4+} ratio.
- Optimal $NaBH_4$ concentration (6 mmol/L) yields superior ORR performance and stability.
- Controlled oxygen vacancy creation is crucial for optimising OMS(2) electrocatalysts for ORR.
- The modified catalyst (6 $NaBH_4$-OMS(2)) shows improved electrochemical surface area and near complete four-electron transfer during ORR.
- The study emphasises the significance of strategically engineering oxygen vacancies to improve the catalytic efficiency and long-term stability of OMS-2 for oxygen reduction.

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