Multiphase manganese oxides with micron cage structure as high-performance cathode material for AZIBs

Tingting Li, Ruisong Guo*, Leichao Meng, Xiaohong Sun, Yang Li

Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, 300072, China. (*rsguo@tju.edu.cn)

Introduction

- Mn_3O_4 has good tolerance to long cycles and prevents agglomeration of δ-MnO_2.
- The porous structure has a high specific surface area and abundant interior space.
- Micron cage structure shortens Zn^{2+}/e^- transport paths.
- The heterostructure and N-doping improve the conductivity of Mn-based materials.
- N-Mn_3O_4/MnO outputs a capacity of 127.7 mAh g^{-1} at 10 A g^{-1} for 2500 cycles.

Results

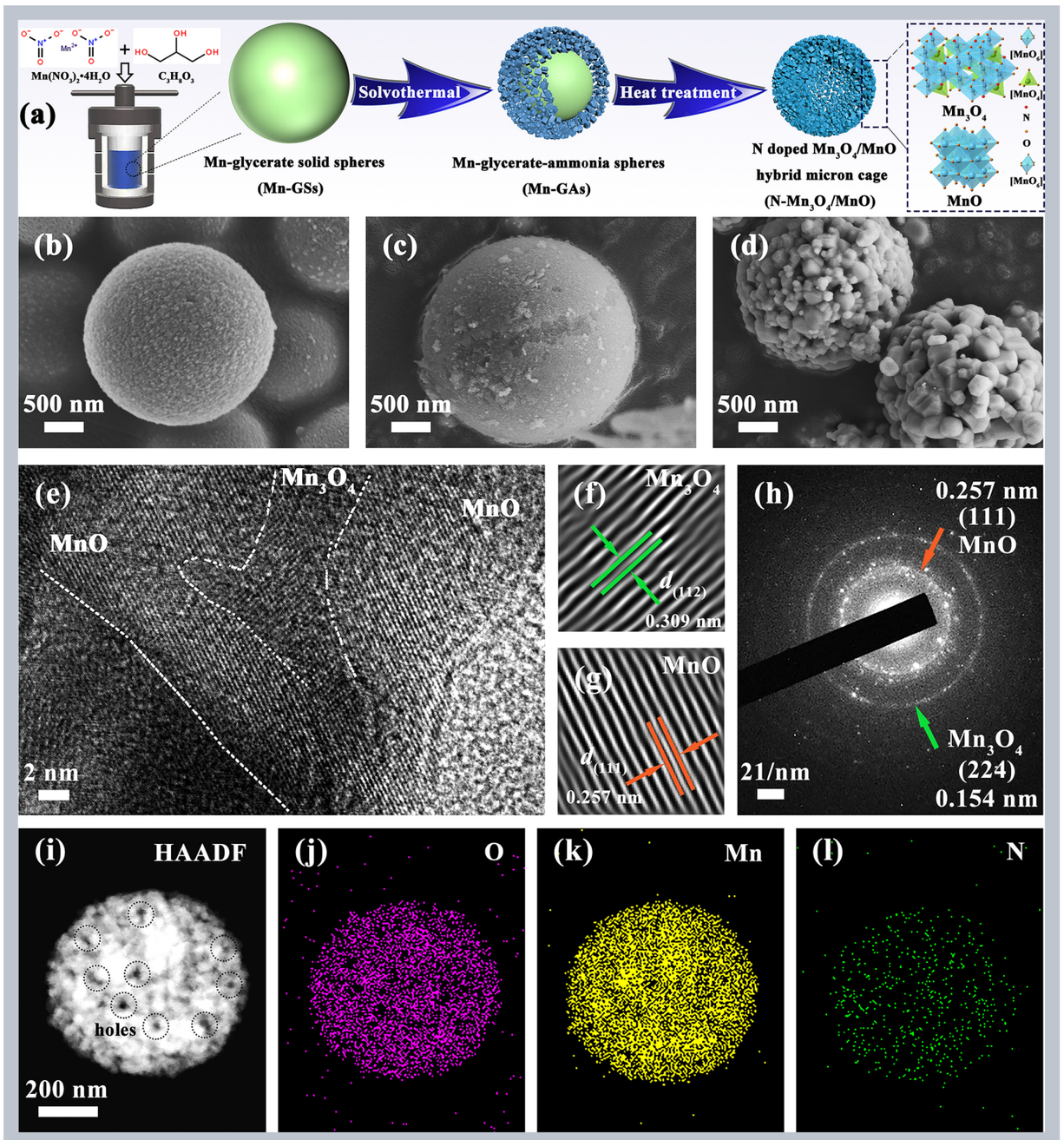

Fig. 1 Schematic illustration of synthesis of the N-Mn_3O_4/MnO hybrid (a). FESEM images of the Mn-GS, Mn-GA and N-Mn_3O_4/MnO powders (b-d), and HRTEM image and EDS images of the N-Mn_3O_4/MnO powders (e-l).

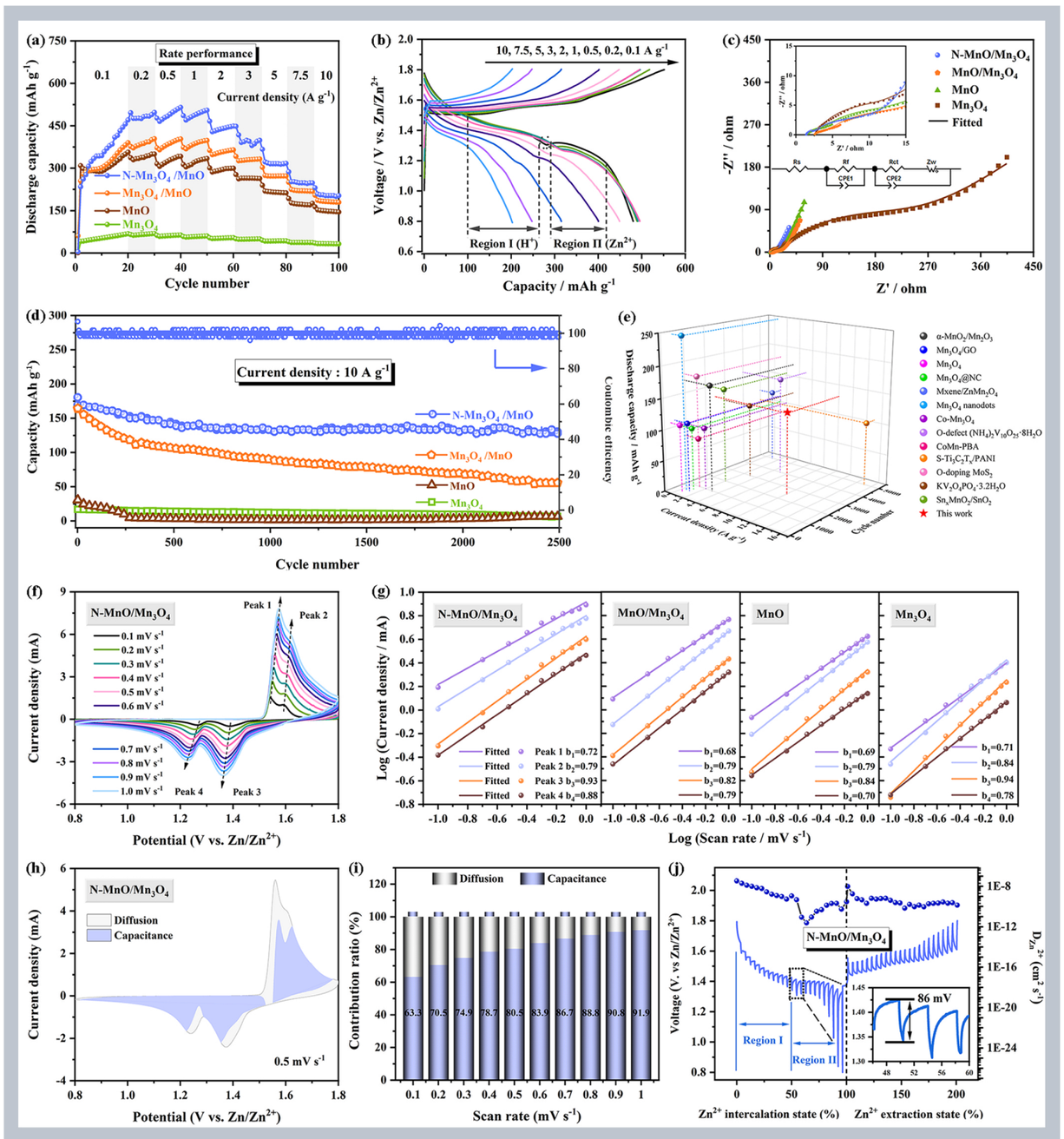

Fig. 2 Rate capability of all cathodes (a), Galvanostatic charge/discharge curves of N-Mn_3O_4/MnO cathode at different current densities (b), EIS patterns of all cathodes before cycle (c), Cyclic performances at 10 A g^{-1} (d), Comparison of cyclic performances of N-Mn_3O_4/MnO cathodes for AZIBs from this work (e), CV curves of N-Mn_3O_4/MnO electrode at various scan rates (f), Corresponding linear fits of the peak currents of all cathodes at various scan rates (g), Capacitive contribution at 0.5 mV s^{-1} (h), Contribution ratio of diffusion/capacitive controlled capacities at various scan rates (i) and GITT voltage profiles of the N-Mn_3O_4/MnO cathodes (j).

Reaction mechanism

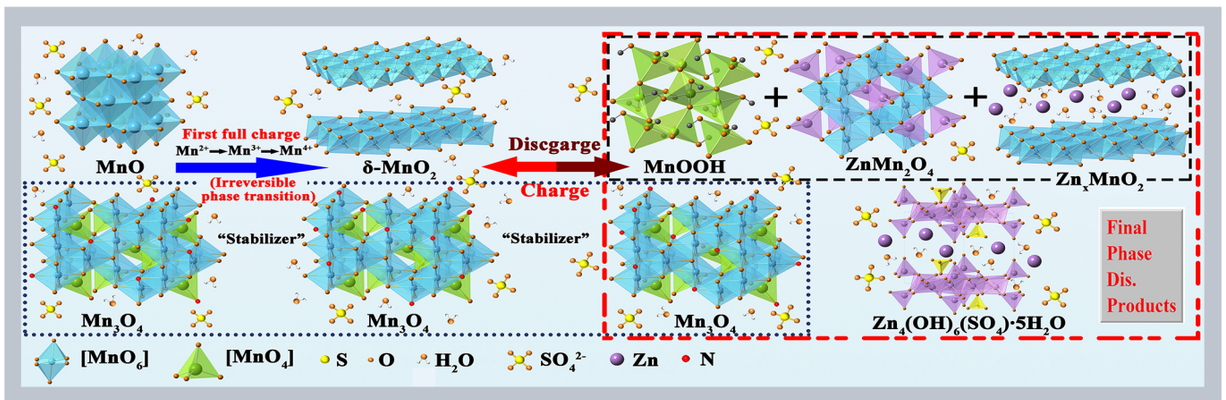

Fig. 3 Schematic illustration of phase transition mechanism

Conclusions

The porous structure of micron cage has high specific surface area, abundant interior space, reduced ion-diffusion path and large electrolyte/electrode contact area. The charge storage mechanism of H^+/Zn^{2+} co-insertion reaction. N-Mn_3O_4 phase acts as a stabilizer, which can alleviate the stress caused by both Zn^{2+}/H^+ insertion into MnO crystal and the great phase transition. The N/C doping increases the diffusion coefficient, inhibits the Jahn-Teller effect of Mn(III), accelerates the charge transfer and improves the conductivity. N-Mn_3O_4/MnO outputs a capacity of 127.7 mAh g^{-1} after cycling for 2500 at 10 A g^{-1}. Therefore, such an energy storage mechanism provides the N-Mn_3O_4/MnO//Zn batteries with superior rate capability and stable cycling performance as well.