

Electronic Supplementary Information (ESI)

NiMn₂O₄ as an Efficient Cathode Catalyst for Rechargeable Lithium-air Batteries

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Material Synthesis

NiMn₂O₄ particles were synthesized with two different routes. One is the coprecipitation method followed by heat-treatment at high temperature similar to that by Ma et al.¹ to prepare porous and hollow-structured NiMn₂O₄ microspheres. The specific procedure was as follows: 1.67 mmol Ni(NO₃)₂·6H₂O, 3.33 mmol MnSO₄·H₂O and 35 ml ethanol were dissolved in 350 ml distilled water with vigorous stirring, 40 mmol NH₄HCO₃ dissolved in 350 ml distilled water was then added. The obtained solution was kept at 45 °C for 9 h with vigorous stirring. The precipitate was then collected by filtration, washed with distilled water and dried at 60 °C overnight in vacuum. The obtained carbonate precursor was heat-treated in air at 600 °C for 3 h and then at 900 °C for 2 h to prepare the NiMn₂O₄ microspheres. The other route was the ball milling method and the subsequent heat-treatment. 2.675g Ni(Ac)₂·4H₂O and 5.629g Mn(Ac)₂·4H₂O was mixed and ball milled for 2 h at 350 rpm in a planetary ball milling machine (Pulverisett 6) with agate vessels. Then the powders were calcined in air at 800 °C for 6 hours to

synthesize the NiMn₂O₄ particles.

Material Characterization

Phase components in the as-prepared NiMn₂O₄ particles were characterized by powder X-ray diffraction (XRD) using a Bruker D8 advance diffractometer. Morphologies of the NiMn₂O₄ particles were analyzed with the Philips-FEI Sirion scanning electron microscope (SEM) and the JEOL 2100F transmission electron microscope (TEM). Phase components and morphologies of the cathodes at various states, including fresh, discharged and recharged, were captured with XRD and SEM, respectively. Considering the magnetic feature of nickel foam could cause possible damage to the SEM instrument, the cathodes for the morphology study was with carbon paper as the substrate.

Electrochemical Measurements

To evaluate the electrochemical performance of the prepared NiMn₂O₄ particles as cathode catalysts in Li-air batteries, the batteries were fabricated by spraying the slurry, which was made from NiMn₂O₄ as catalyst, Super P carbon as conductive agent, and polytetrafluoroethylene (PTFE) as binder with a weight ratio of 3:6:1 in ethanol, evenly onto nickel foam (12 mm in diameter) as the substrate with a paint spray gun. The loading of materials (catalyst, Super P carbon, and PTFE) in each cathode was controlled at 0.5 mg. For comparison, the pure carbon cathodes without catalysts were fabricated with the slurry made of 90 wt.% Super P carbon and 10 wt.% PTFE using the same procedure. After being dried at 120 °C in vacuum overnight, an as-prepared cathode, a lithium metal anode, a glass fiber separator, and an electrolyte of 1 M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) in TEGDME (tetraethylene glycol dimethyl ether) were used together to assemble a Li-air battery with a self-modified Swagelok cell² in an argon-filled glovebox with oxygen and water contents of less than 0.1 ppm. The cyclic voltammetry (CV) curves for NiMn₂O₄ based cathodes were recorded using a CHI 750a electrochemical potentiostat/galvanostat within the voltage range of 2.0-4.5 V (*vs.* Li metal) at a potential scanning rate of 0.5 mV s⁻¹. The discharge-charge performance of the batteries was measured using a LAND CT2001A battery testing system with a discharge cutoff voltage 2.0 V. All the measurements were conducted in a 1.0 atm O₂ atmosphere at room

temperature. The specific capacity and current density were calculated based on the amount of Super P carbon in the cathode.

Results and Discussion

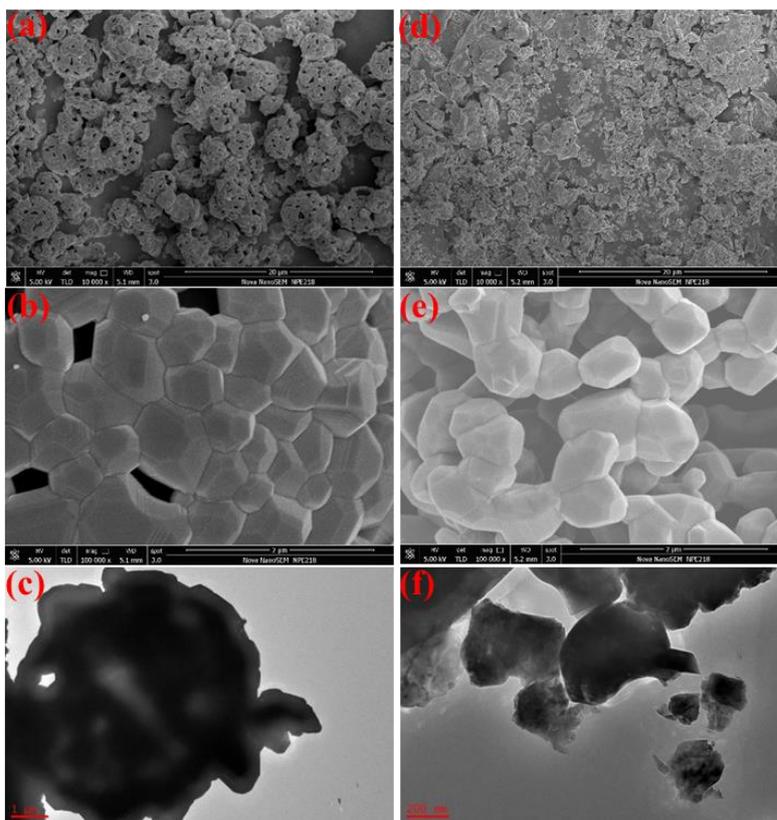
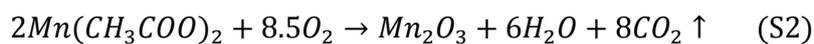
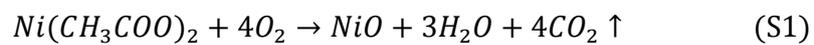


Fig. S1 SEM (a, b, d, e) and TEM (c, f) images of NiMn₂O₄-PH (a-c) and NiMn₂O₄-FT (d-f)

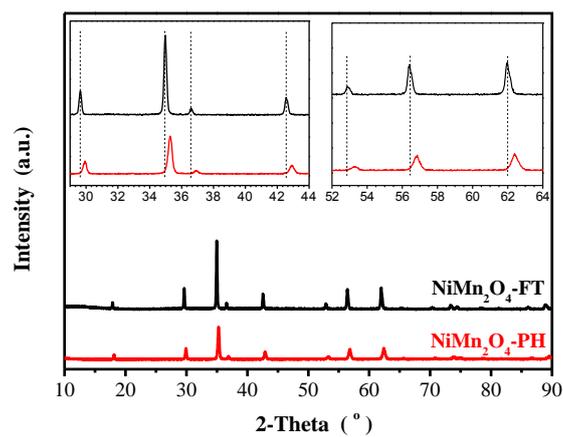


Fig. S2 XRD patterns of NiMn₂O₄-PH and NiMn₂O₄-FT

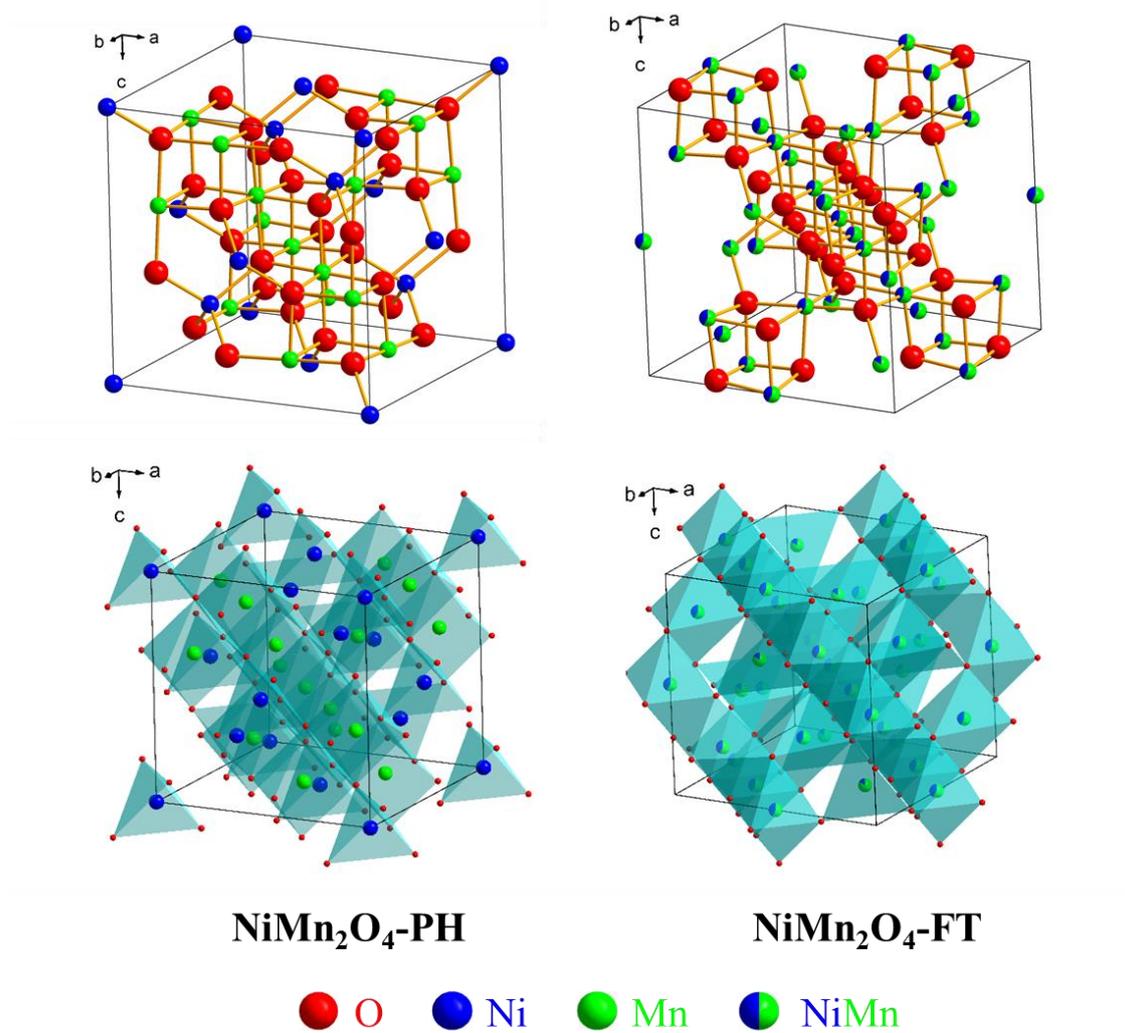


Fig. S3 Crystallographic structure of NiMn₂O₄-PH and NiMn₂O₄-FT

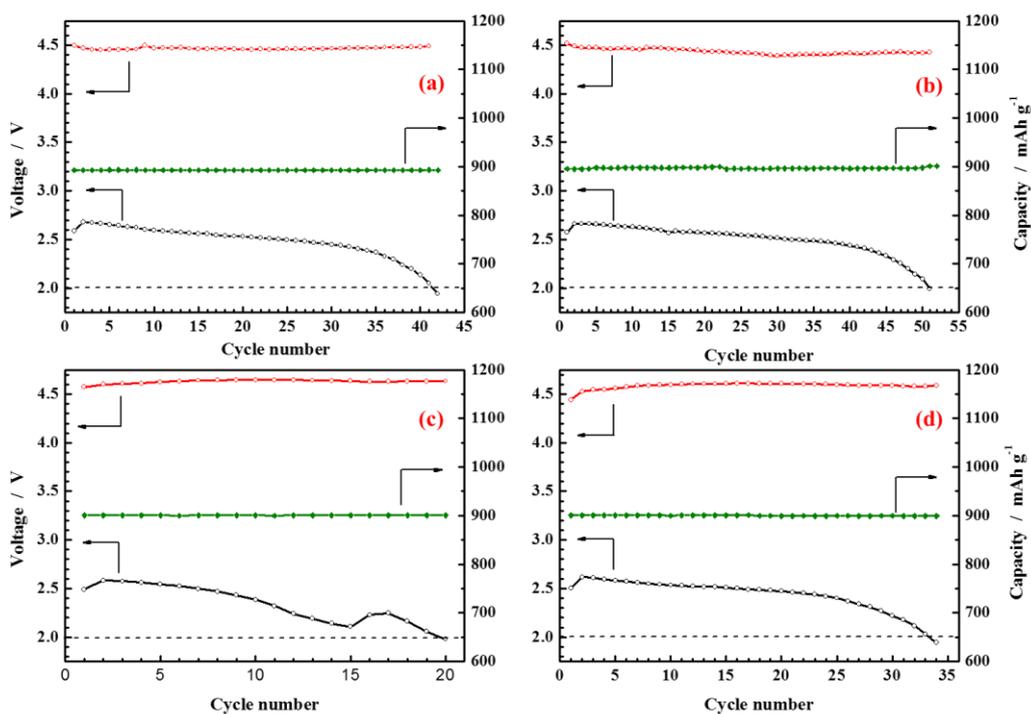


Fig. S4 Cycling performance of Li-air batteries with NiMn₂O₄-PH (a, c) and NiMn₂O₄-FT (b, d) based cathodes at a current density of 150 mA g⁻¹(a, b), 400 mA g⁻¹(c, d) with a controlled capacity of 900 mAh g⁻¹

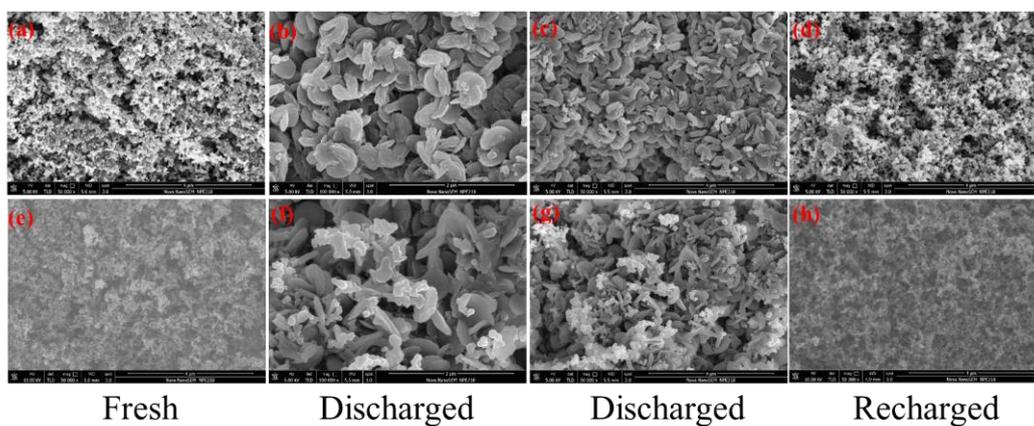


Fig. S5 SEM images of NiMn₂O₄-PH (a-d) and NiMn₂O₄-FT (e-h) based cathodes at various states

Reference

- 1 Z. Ma, X. Yuan, L. Li, Z. F. Ma, L. Zhang, L. Mai and J. Zhang, *J. Power Sources*, 2015, 291, 156.
- 2 Z. Ma, X. Yuan, H. D. Sha, Z.-F. Ma, Q. Li, *Int. J. Hydrogen Energy*, 2013, **38**, 11004.