Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A stable tunnel-type $NaGe_{3/2}Mn_{1/2}O_4$ anode for Na-ion battery

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Supplementary Methods

Synthetic procedures

Both of NGMO and NGO were prepared by solid-state method, in which commercial sodium carbonate, manganese sesquioxide and germanium dioxide were used as starting chemicals to fabricate precursor. The molar ratio of Na:Ge:Mn to NGMO was 2:3:1 (Na:Ge is 1:2 for NGO). An excess of 5 % Na_2CO_3 was added to compensate the loss of Na. All the materials were ball-milled for 15 hours at 200 rpm. Then the obtained powder was heated in the form of the pellets, first preheated at 650 °C for 48 hours and following heated at 750 °C for another 120 hours in Ar atmosphere. X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500 XRD (Cu Kα radiation) in the 2θ range of 10-60°. The morphology and structure, characterized by SEM (Verios 460L, FEI) and TEM (Tecnai G2, FEI). XPS (ESCALAB 250Xi) simultaneously was conducted to analyze the valence states difference, the cycled electrodes of NGMO and NGO were etched in Ar atmosphere for 250 s.

Electrochemical measurements

Electrochemical properties were studied by the measurements for CR2032-type half cells. The working electrodes were composed of 70 wt% NGMO or NGO, 20 wt% conductive agent of acetylene black and 10 wt% carboxyl methyl cellulose sodium, in which Na metal was used as counter electrode and 1 mol L^{-1} $NaClO_4$ dissolved in EC:DEC (1:1 in volume ratio) as an electrolyte. The mass loading of NGMO/NGO were approximately 0.89 mg cm^{-2}. Coin cells were studied by LAND CT2001A battery test system. EIS was measured with amplitude of 5 mV in a frequency range of 0.01 Hz-100 kHz.

Supplementary Figures

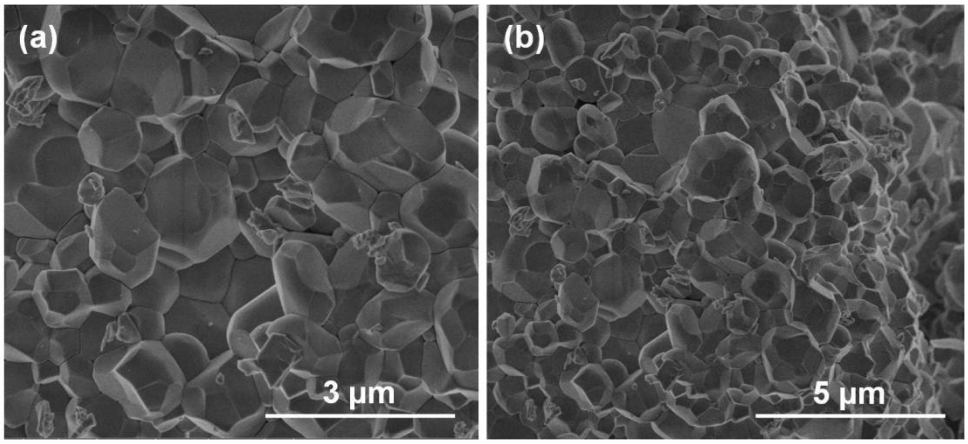

Fig. S1 (a), (b) are the different resolutions SEM images of NGO.

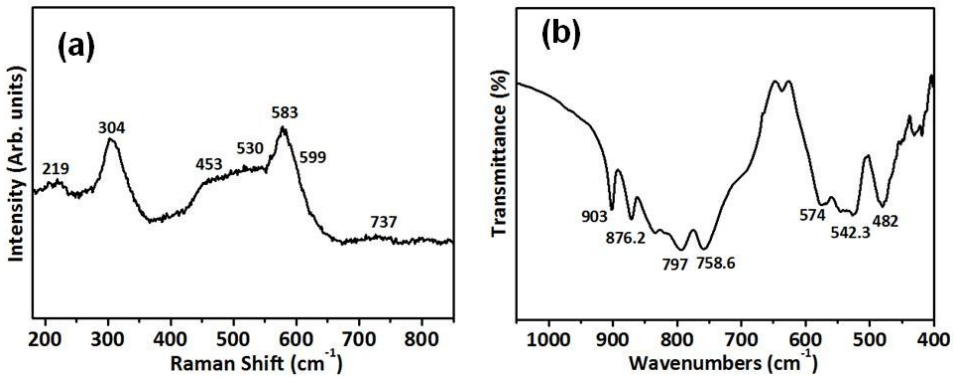

Fig. S2 (a) Raman and (b) IR spectras of NGMO.

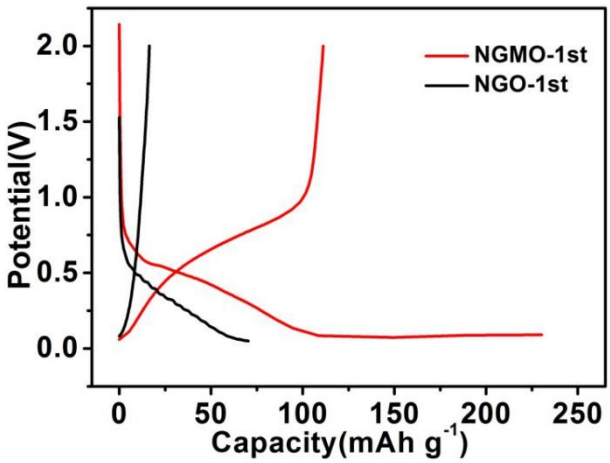

Fig. S3 The 1st discharged curves of NGMO and NGO.

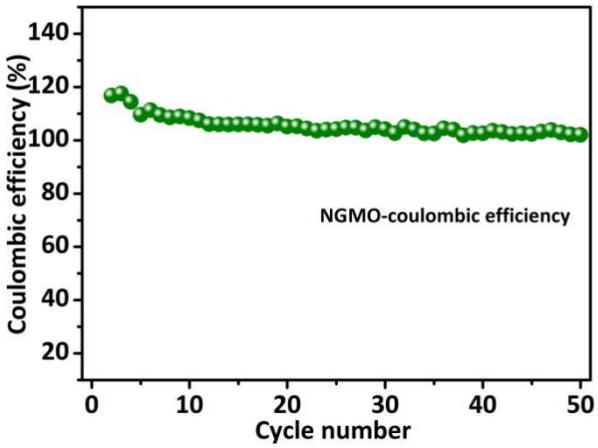

Fig. S4 The coulombic efficiency of NGMO in the first 50 cycles.

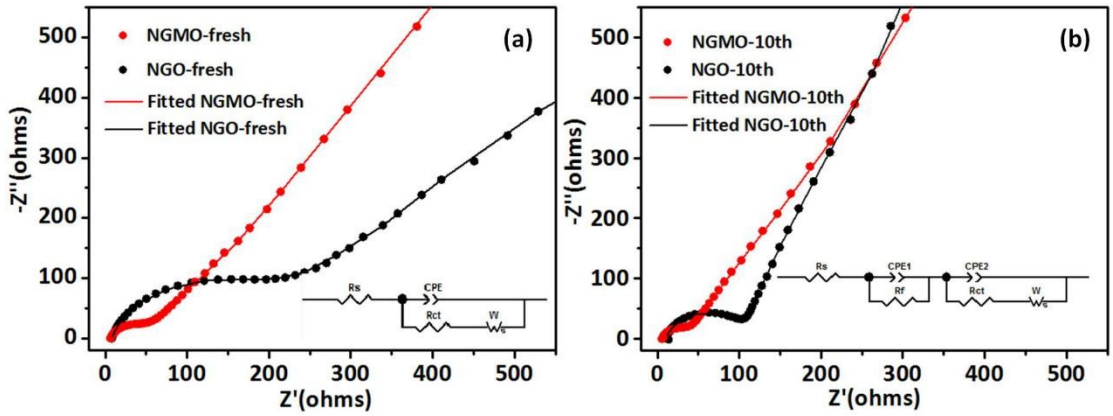

Fig. S5 The fitting results of EIS, inside is the equivalent circuit model. NGMO and NGO (a) Fresh states, (b) 10th discharged cells.

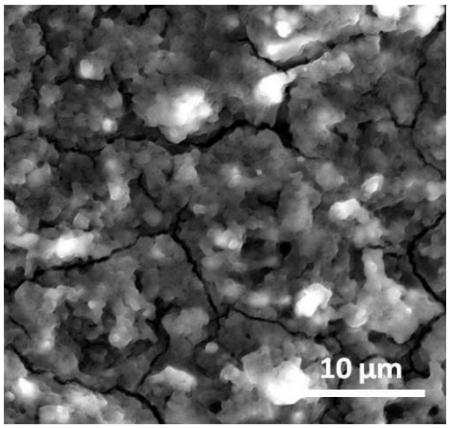

Fig. S6 Long cycle performance and SEM image of discharged electrode of NGMO.

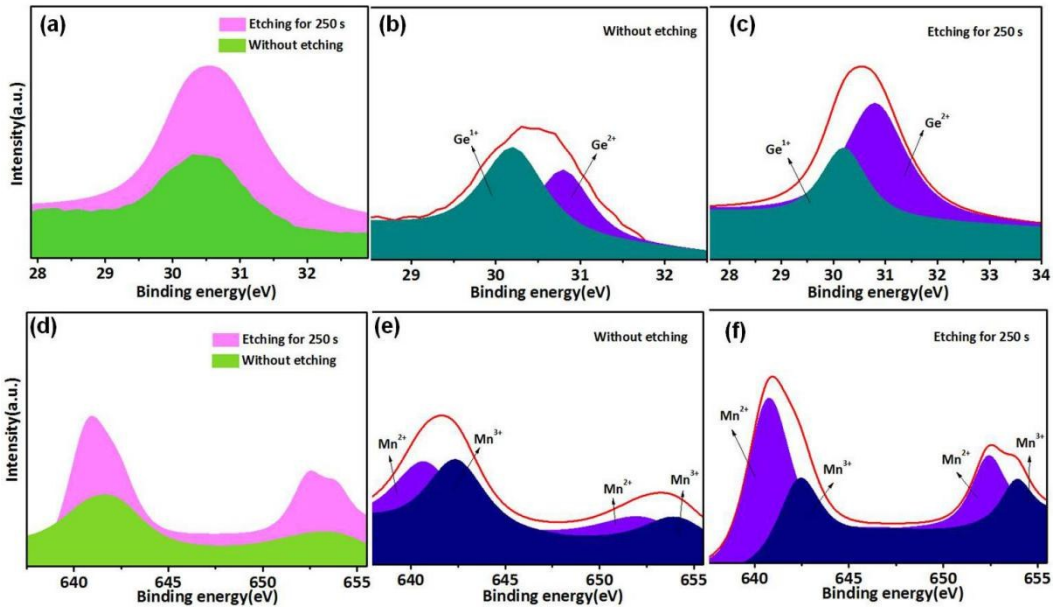

Fig. S7 XPS spectra of 150th cycled electrode of NGMO without and with etching for 250 s by Ar plasma, (a) Ge 3d core level, (b) and (c) are the chemical valence states analysis of two electrodes, respectively. (d) Mn 2p core level, (e) and (f) are the chemical valence states analysis of two electrodes, respectively.

Table 1 Atomic percentage of each element in NGMO.

Element	Atom%
Na	30.58
Ge	55.04
Mn	14.48
Total	100.00

Table S2 Fitting results of EIS.

Parameters	R_s	R_{ct}
NGMO-fresh	6.541	51.34
NGO-fresh	8.21	166.9
NGMO-10th	5.787	37.3
NGO-10th	10.81	97.43