Excellent electrochemical performance of NiV₃O₈/natural graphite anodes via novel in situ electrochemical reconstruction

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Experimental

Fabrication procedure

The chemicals were analytical grade and purchased from Shanghai Chemical Reagents. Natural graphite was obtained from Yichang Hengda graphite company (99.9%). In a typical procedure, 3 mmol V₂O₅, 2 mmol Ni(CH₃COO)₂•4H₂O and 2 mmol glucose were dissolved in 30 ml distilled water. After stirring for 20 minutes, the homogeneous yellowy suspension was transferred into a 50 ml teflonlined autoclave, reacting at 160 °C for 24 h. The final products were washed by distilled water and ethanol both four times and dried in an oven, then sintered in air atmosphere at 400 °C for 5h.

Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-Ray powder diffraction (Rigaku Ultima IV Cu K α radiation λ =1.5406 Å), field-emission

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scanning electron microscopy (FE-SEM JSM 7500F, JEOL) and transmission electron microscopy (TEM, FEI, Tecnai G2 F30).

Electrochemical characterization

For fabricating lithium ion battery, the as-prepared NiV₃O₈ was firstly mixed with natural graphite with weight ratio of 1:1 in a 100 ml agate mortar and manually rubbed for 0.5 h (defined as NiV₃O₈/NG). Then the mixture was further mixed with acetylene black and sodium alginate (SA, dissolved in deionized water, 0.02 g ml⁻¹) with weight ratio of 8:1:1 and coated on copper foil. The coated copper foil was cut into disc electrode with a diameter of 14 mm using a punch. Coin-type cells (2025) of Li/1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/disk electrode were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, H₂O<1.0 ppm, O₂<1.0 ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. Galvanostatic charge/discharge test was characterized on a multichannel battery test system (LAND CT2001A) in the voltage region between 0.02 and 3 V. The weight of both NiV_3O_8 and NG were considered as the total weight of active material on Cu foil when calculating the specific capacity of the electrode. The cyclic voltammetry measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of $0.2 \text{ mV} \text{ s}^{-1}$ between 0 and 3 V.



Fig.S1 (a) CV curves for pure NiV_3O_8 and (b) XRD patterns of the electrode under different discharge and charge state.

XRD patterns of pure NiV₃O₈ electrode under different states in the initial cycle was studied to further understand the electrochemical behavior of NiV₃O₈ in cycling. The charge and discharge state was selected according to the initial CV curve as shown in Fig. s1(a). As seen, when discharging to 2.18 V, new diffraction peaks near 18.8°, 25.9° and 31.5° appear, corresponding to the (010), (100) and (400) faces of LiV₂O₅ (JCPDS, no. 34-1273). Meanwhile, the diffraction peaks of NiV₃O₈ disappear, which suggest an amorphization process accompanied by the phase transition from NiV_3O_8 to LiV₂O₅ and other nickel vanadium oxide. According to the molecular formula, one can deduce that the electrochemical reaction during the initial discharging process can be describes as $NiV_3O_8 \rightarrow LiV_2O_5 + NiVO_3$. The insertion of lithium ions accompany by the reduction of V^{5+} , which can be reflected by the formation of LiV_2O_5 , whereas the valence state of V in NiVO₃ was in accordance with that of NiV₃O₈. The generation of Li_xV₂O₅ and Co that accompanied by an amorphization process during the lithiation of $Co_3V_2O_8$ has been testified by Yang et al. [1]. Here in this paper, it is proposed that the sequential generation of Li_xV₂O₅ accompanied by the decomposition of NiVO₃ will occur in the subsequent discharging. However, the amorphous state makes it difficult to distinguish the detailed discharging mechanism.



In the charging process, the amorphous state of the NiV₃O₈ electrode was kept.

Fig. s2 Long-life performance of the NiV_3O_8/NG electrode versus the theoretical capacity of graphite.



Fig. s3 SEM image of fresh NiV₃O₈/NG electrode.

[1] G.Z. Yang, H. Cui, G.W. Yang, C.X. Wang, ACS Nano, 8 (2014) 4474-4487.