Excellent electrochemical performance of NiV$_3$O$_8$/natural graphite anodes via novel in situ electrochemical reconstruction

Shibing Ni$^{a, b1}$, Jianjun Ma$^{a, c}$, Jicheng Zhang$^{a}$, Xuelin Yang$^{a, b2}$, Lulu Zhang$^{a, b}$

$^a$ College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China
$^b$ Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University
$^c$ College of mechanical and Power Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China

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 V$_2$O$_5$, 2 mmol Ni(CH$_3$COO)$_2$•4H$_2$O 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 Kα radiation $\lambda=1.5406$ Å), field-emission...
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 NiV$_3$O$_8$ 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 NiV$_3$O$_8$/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 LiPF$_6$ 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, H$_2$O<1.0 ppm, O$_2$<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$_3$O$_8$ 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 mV s$^{-1}$ between 0 and 3 V.
Fig. S1 (a) CV curves for pure NiV$_3$O$_8$ and (b) XRD patterns of the electrode under different discharge and charge state.

XRD patterns of pure NiV$_3$O$_8$ electrode under different states in the initial cycle was studied to further understand the electrochemical behavior of NiV$_3$O$_8$ 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 LiV$_2$O$_5$ (JCPDS, no. 34-1273). Meanwhile, the diffraction peaks of NiV$_3$O$_8$ disappear, which suggest an amorphization process accompanied by the phase transition from NiV$_3$O$_8$ to LiV$_2$O$_5$ 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$_3$O$_8$ $\rightarrow$ LiV$_2$O$_5$ + NiVO$_3$. The insertion of lithium ions accompany by the reduction of V$^{5+}$, which can be reflected by the formation of LiV$_2$O$_5$, whereas the valence state of V in NiVO$_3$ was in accordance with that of NiV$_3$O$_8$. The generation of Li$_x$V$_2$O$_5$ and Co that accompanied by an amorphization process during the lithiation of Co$_3$V$_2$O$_8$ has been testified by Yang et al. [1]. Here in this paper, it is proposed that the sequential generation of Li$_x$V$_2$O$_5$ accompanied by the decomposition of NiVO$_3$ 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 NiV₃O₈/NG electrode versus the theoretical capacity of graphite.](image)

![Fig. s3 SEM image of fresh NiV₃O₈/NG electrode.](image)