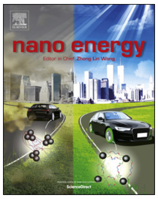
Nano Energy 51 (2018) 83–90

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen



Full paper

A current collector covering nanostructured villous oxygen-deficient NiO fabricated by rapid laser-scan for Li-O_2 batteries

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ARTICLE INFO

Keywords:
NiO
Oxygen vacancy
Laser-scan
Current collector
Li-O_2 battery

ABSTRACT

Non-aqueous Li-O_2 batteries attract extensive attention because of their ultra-high theoretical specific energy density. However, the high charge potential, which induces severe parasitic reactions such as the corrosion of carbon-based catalysts and metal current collectors, is one of the biggest challenges currently. Herein, a current collector of Ni foam covering nanostructured villous NiO with oxygen vacancies ($NiO_{1-\delta}$) was fabricated by a fast laser-scan technique. The modified $NiO_{1-\delta}$ based current collector presented superior stability and comparable electrocatalytic activity. It delivered a discharge capacity of about 500 mAh g^{-1} and a low charge potential of 3.84 V in a Li-O_2 cell in the absence of catalysts. And this cell could maintain 73.5% of the initial capacity after 100 full discharge-charge cycles. Density functional theory (DFT) calculations verified that the improved electrocatalytic activity mainly derived from the introduction of oxygen vacancies in $NiO_{1-\delta}$. It improved the electronic conductivity for rapid electron transfer as well as served as active sites to bind O_2 and oxygen-containing intermediates (eg. LiO_2) for electrochemistry reactions. This work gives a rapid and easily mass-produced method to fabricate a stable and activated current collector for Li-O_2 batteries.

1. Introduction

Owing to their extremely high theoretical specific energy density (~3500 Wh kg^{-1}), rechargeable non-aqueous lithium-oxygen (Li-O_2) batteries have captured worldwide attention [1–5]. They are promising to meet the power requirements of electric vehicles and smart grids, taking the place of traditional Li-ion batteries. Typically, in a Li-O_2 battery system, its operation depends on the reversible formation and decomposition of Li_2O_2 (Eq. (1)) [6–8]. However, lots of challenges must be addressed before their usage in practical applications. The primary challenge is the high charge potential in oxygen evolution reactions (OER) [9–13]. It has resulted in the low round-trip efficiency, detrimental degradation of electrolyte and poor cycle life. Therefore, multitudes of research efforts have been focused on combining effective catalysts and porous electrode structures to reduce the charging overpotential for non-aqueous Li-O_2 batteries [14–16].

$$2Li^{+} + O_2 + 2e^{-} \leftrightarrow Li_2O_2, \qquad E^0 = 2.96V \tag{1}$$

Based on previous reports, carbon based catalysts and carbon paper/cloth current collectors are widely applied in Li-O_2 batteries because of their high surface area, excellent electronic conductivity and superior oxygen reduction reaction (ORR) catalytic performance [17–19]. However, many studies demonstrated that carbon is susceptible to be corroded by the attack of reaction intermediated radicals and can actively promote the decomposition of electrolyte during cycling [17–20]. Hence, it is of necessity to elaborately design carbon-free cathodes, including carbon-free catalysts and current collectors, for Li-O_2 batteries to circumvent these parasitic reactions. Among varieties of carbon-free current collectors, Ni metal is most widely applied [21–24], which exhibits higher electronic conductivity over carbonaceous materials and metal oxides [25,26]. Nonetheless, different from carbon collectors, Ni metal shows little catalytic activity and makes no contribution to the battery performance. Besides, Ni metal is easily

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https://doi.org/10.1016/j.nanoen.2018.06.043
Received 16 April 2018; Received in revised form 15 May 2018; Accepted 12 June 2018

oxidized inherently as a kind of active metals [27], especially when it is applied in an O_2-rich system with high oxidation potential. It has been reported that NiO possesses good activity towards the decomposition of both Li_2O_2 and Li_2CO_3 [21,28,29]. However, the electronic conductivity of NiO is inferior, which will undoubtedly increase the interface impedance and prevent the rapid charge transfer, leading to a high overpotential. Fortunately, in a recent literature, Ling et al. introduced oxygen vacancies into metal oxides, which is an effective way to significantly improve their electronic conductivity [30]. As a consequence, creating a covering layer of NiO with oxygen vacancies ($NiO_{1-\delta}$) on the Ni metal current collector is proposed to enhance its stability, electroconductivity and electrocatalytic activity in Li-O_2 batteries.

In the present work, we developed a one-pot fabrication of nanostructured villous $NiO_{1-\delta}$ layer grown on Ni foam collector directly by the fast laser-scan technique. The surface of Ni metal was protected effectively by the layer of $NiO_{1-\delta}$ nano-villi. Particularly, the electroconductivity and electrocatalytic activity of the whole Ni collector were promoted significantly. DFT calculations verified that the improved electrochemical performance mainly stemmed from the introduction of oxygen vacancies in NiO. It not only improved the electronic conductivity for rapid electron transfer [30], but also served as active sites to bind O_2 and oxygen-containing intermediates (eg. LiO_2) for electrochemistry reactions [31–35]. Moreover, a RF magnetron sputtering method was employed to deposit Ru nanoparticles onto the modified Ni collector to construct a self-standing carbon-free cathode. And superior discharge-charge performance with lower charge overpotential was obtained in Li-O_2 batteries.

2. Experimental section

2.1. Materials preparation

Ni foam was put on the substrate of the laser processing device (BX4II-E, Senged Laser). Then, it was irradiated by a linearly polarized ns laser with wavelength of 532 nm, repetition rate of 50 kHz, pulse duration of 12 ns and pulse energy of 0.4 mJ. A two mirror galvo scanner with an F-theta objective lens (f = 160 mm) was used to focus and scan the laser beam in the x-y directions. Here, 600 mm s^{-1} was adopted to tune the content of the oxide at the surface of Ni foam, which is the top irradiation speed we can carry out to keep the structural integrity. Besides, laser-scan speeds of 200 and 400 mm s^{-1} were also applied for comparison. After laser-scan treatments, the Ru nanoparticles were deposited on the surface of Ni foam by RF magnetron sputtering in 1 min with a constant power of 100 W. Pristine Ni foam functionalized with Ru nanoparticles without irradiation was also prepared. The process gas was pure argon at a pressure of 2.0 Pa, which was introduced into the chamber with a flow rate of 120 sccm. The Ni foam was positioned straight to the Ru target at a target-substrate distance of about 20 cm.

2.2. Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on a Hitachi S-8010 (Tokyo, Japan) and JEOL JEM-2100 (Tokyo, Japan), respectively. The states of surface elements were characterized using X-ray photoelectron spectroscopy (XPS) spectra recorded by a Thermo Fisher Scientific Model K-Alpha spectrometer equipped with Al Ka radiation (1486.6 eV). Tauc plots were obtained based on the UV–Vis absorption spectra, which were acquired on a Shimadzu UV-3600 ultraviolet-visible spectrophotometer. The NiO contents were calculated based on the weight loss during the reduction of NiO into Ni under Ar/H_2 gas (H_2, 10 vol%) with a thermogravimetric analyzer (TG, Netzsch STA-449F3).

2.3. Electrochemical measurements

The Ni foam, LS-Ni foam, Ru@Ni foam and Ru@LS-Ni foam were used directly without any additional binder or conductive agent. CR2032-type coin cells with holes for oxygen-transfer were assembled in a glovebox filled with dry Ar to evaluate the electrochemical performance. And all the electrode material was dried at 80 ℃ overnight before assemblage. Tetraethyleneglycol dimethyl ether (TEGDME) (from Aldrich) mixed with $LiCF_3SO_3$ in a molar ratio of 4:1 was used as the electrolyte. LAND 2001A Battery Testing Systems (Wuhan LAND electronics Co., Ltd, P.R. China) were used for electrochemical performance tests. The capacities of the Li–O_2 batteries were normalized by the mass of NiO and the current densities applied were 100 mA g^{-1}. Electrochemical impedance spectroscopy (EIS) Nyquist plots were measured with a frequency range of 100 kHz to 0.1 Hz and a scan rate of 10 mV s^{-1} by an electrochemical station (CHI440C, Shanghai Chenhua Co., Ltd, P.R. China). Mott-Schottky (M-S) tests were carried out by an electrochemical station (Zahner IM6) at a frequency of 1000 Hz in a typical three-electrode system with a saturated calomel reference electrode and a platinum plate counter electrode. And the electrolyte applied was the buffer solution of potassium phosphate (0.2 M, pH = 7).

2.4. Theoretical calculations

Spin-polarized DFT calculations were performed by using the Vienna ab initio simulation package (VASP) [36] with the projector augmented wave (PAW) method [37] and Perdew, Burke and Ernzerhof (PBE) functional [38]. The Hubbard-type U correction of Ni was taken into consideration and set to be 6.2 eV [39,40]. The most stable surface (100) of NiO was selected to be catalyst surface [41]. A six layers' slab with 2 × 1 lateral cells and a 10 Å vacuum along the z-direction was used to model the surface system. Cutoff energy was set 500 eV for the plane-wave basis set in all calculations. The Brillouin zone was sampled by 4 × 8 × 1 Gamma centered mesh. Both layer thickness and k-point mesh here were tested to achieve a convergence of total energy within 0.01 eV. The top four layers of the slab were allowed to relax, the other two layers at bottom were fixed to mimic a bulk region. The convergence criteria for structural optimization was set to 0.1 eV/Å in force, while for the electronic step was set to 10^{-4} eV.

The adsorptions of O_2 and LiO_2 molecules on NiO surfaces as well as the electronic properties of slabs have been calculated. Herein adsorption energy ΔE is considered as the descriptor of binding strength. A negative value of ΔE suggests favorable adsorption, and it is determined by using Eq. (2),

$$\Delta E_M = E(NiO + M) - E(NiO) - E(M) \tag{2}$$

where $E(NiO + M)$ and $E(NiO)$ represent the total energy of NiO system with and without the molecule M adsorbed on surface, respectively. Here M can be LiO_2 or O_2, and $E(M)$ represents the total energy of LiO_2, or gas phase O_2 molecule. Table S1 shows the calculation results of O_2 and LiO_2 adsorption.

3. Results and discussion

Herein, Ni foam was selected as the substrate material and treated by an elaborate method of laser-scan. Compared with other Ni metal collectors, Ni foam possesses 3D macroporous skeletons that favorably facilitate the rapid diffusion of O_2 and the effective infiltration of electrolyte for the whole energy conversion process. The laser treatment of Ni foam with size of 5 cm × 5 cm was completed within 7 min at the fast laser-scan speed (600 mm s^{-1}), clearly demonstrating the high preparation efficiency. And the color of Ni foam changed from silver white to deep black after laser-scan (Fig. 1a). Scanning electron microscopy (SEM) was utilized to characterize the architectures of Ni foam after laser-scan (denoted as LS-Ni foam) (Fig. 1b-d). It can be seen