



Short communication

High capacity Na–O₂ batteries with carbon nanotube paper as binder-free air cathodeZelang Jian^a, Yong Chen^{a,b}, Fujun Li^{a,c}, Tao Zhang^a, Chang Liu^d, Haoshen Zhou^{a,*}^aEnergy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba 305-8568, Japan^bKey Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan University, 58 Renmin Road, Haikou 570228, China^cDepartment of Engineering, The University of Tokyo, Building 5-607, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan^dShenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

HIGHLIGHTS

- CNT paper was firstly introduced to Na–O₂ battery.
- The cell showed high capacity and small potential gap.
- Na₂O₂·2H₂O is identified as the main crystalline discharge product.

ARTICLE INFO

Article history:

Received 30 September 2013

Received in revised form

21 November 2013

Accepted 26 November 2013

Available online 8 December 2013

Keywords:

Na–O₂ battery

Carbon nanotube paper

Binder-free

Cathode

ABSTRACT

A carbon nanotube paper without any binders and additives was directly used as the catalyst for Na–O₂ batteries. Corresponding electrochemical performances were investigated. A large discharge capacity can be high up to 7530 mAh g⁻¹, which, to the best of our knowledge, is the highest value obtained at the similar current density. The cycling performance of the Na–O₂ battery can be improved with a capacity limit of 1000 mAh g⁻¹. Moreover, the overpotential gap was as small as 200 mV. Na₂O₂·2H₂O is identified by X-ray diffraction (XRD) as the main crystalline discharge product and can be decomposed in the following charging process as revealed by scanning electron microscope (SEM). These results indicate that the CNT paper is a promising cathode for Na–O₂ battery.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronics and are promising energy storage/conversion devices for hybrid electric vehicles (HEV) and electric vehicles (EV) [1]. However, the energy density of LIBs cannot meet the requirements of long-range running, even the theoretical limited of current electrode materials are reached [2]. Li–O₂ batteries (non-aqueous electrolytes) with a high theoretical energy density of about 3505 Wh kg⁻¹, which is comparable with that of gasoline [3,4], may be a solution to electrifying transportation. The current challenges faced by Li–O₂ batteries that limit their practical application are as follows: 1) the potential gap of Li–O₂ batteries is usually higher than 1 V, which induces a low round-trip efficiency, such as 62% in a pure carbon cathode [5]. Even when a precious

metal is used as an electrochemical catalyst, the round-trip efficiency remains lower than 80% [6], which cannot meet the demands of practical propulsion batteries; 2) Li₂O₂, the desirable discharge product of Li–O₂ batteries, can react with carbon cathode at high voltages, which results into decayed cycling performance; [7] 3) the intermediate discharge product LiO₂ readily attacks the binder poly(vinylidene fluoride) (PVDF) to generate LiF and H₂O₂, which further reacts with Li₂O₂ to form LiOH [8]. New battery systems are necessary to overcome such drawbacks.

Recently, Pascal Hartmann and his coworkers [9] have achieved reversible discharging/charging cycles with a low overpotential of less than 200 mV in a Na–O₂ battery. The round-trip efficiency is greatly improved to higher than 90% [9], which is in contrast with that of Li–O₂ batteries. In particular, the charging voltage plateaus of Na–O₂ batteries are significantly lower than that of Li–O₂ batteries. In such a case, carbon corrosion may not be a problem at low voltages, thereby overcoming the first and second drawbacks in Li–O₂ batteries described above. Binder-free materials are

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expected to solve the third drawback. However, only a few studies have focused on Na–O₂ battery, and thus, more experiments should be conducted to understand the issues in the use of Na–O₂ batteries.

Carbon and carbon-based materials have been intensively studied as catalysts for Li–O₂ batteries [5,10]. Carbon nanotubes (CNTs), which have a large surface area, high electric conductivity, and good corrosion resistance, have attracted significant attention and have shown excellent electrochemical performance [11]. In this study, a CNT paper was prepared via a floating catalyst chemical vapor deposition method. The CNT paper was composed of interpenetrating CNTs to improve the electronic conductivity and to create large void spaces inside it. The CNT paper without any binders and additives was used as the catalyst for Na–O₂ batteries. The binder-free CNT paper can be thinner and more porous, considering the mass of the binder in the conventional electrode film. This is important for the storage of the discharge product NaO₂ or Na₂O₂ and the achievable large specific capacity. The corresponding electrochemical performances were investigated.

2. Experimental

The CNT paper was prepared by using benzene as carbon source, ferrocene as catalyst precursor, and thiophene as growth promoter in a tubular furnace [12,13]. Ferrocene is firstly vaporized at about 185 °C, and carried into the reaction tube furnace by H₂ and pyrolyzed to ultrafine Fe catalyst particles above 400 °C. The reaction temperature was maintained at 1200 °C for 1 h and the CNT paper was obtained after natural cooling.

Powder X-ray diffraction (XRD) was performed to characterize the fresh, discharge and charge products on a Bruker D8 Advanced diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The XRD samples, discharged/charged electrodes were taken out from a coin cell and, washed with diethylene glycol dimethyl ether (DEGDME). The samples were enclosed with a thin transparent Kapton film to prevent their exposure to air during testing. Raman spectra were obtained on a Micro Raman spectrophotometer (Ventuno21, JASCO). The morphologies of pristine, discharge and charge electrodes were performed by field emission scanning electron microscopy (FE-SEM, JEOL 6700F).

The CNT paper without any addition of binder or conductive additives was directly used as a cathode in a Na–O₂ battery assembled in a coin cell (CR2032) with holes. The CNT paper was pressed onto a titanium mesh (100 mesh) which served as a current collector. NaSO₃CF₃/DEGDME or NaTFSI/TEGDME (25 μ l) was employed as electrolyte. The electrochemical measurements were performed on Hokudo Denko Charge/Discharge instruments at 25 °C and in the pure O₂ atmosphere.

3. Results and discussion

The CNT paper has a size of about 55 \times 15 mm², as shown in the inset of Fig. 1a. This size can be adjusted depending on the requirement by tuning the collector. Fig. 1a shows the scanning electron microscopy (SEM) image of the CNT paper with a diameter of about 30 nm and a length of several micrometers. The CNTs are interpenetrated together to form a paper. In addition, some small carbon particles attached on the CNTs are observed. The graphitization degree of the as-prepared CNT paper is investigated via Raman spectroscopy, as presented in Fig. 1b. The two peaks located at 1331 and 1581 cm⁻¹ are assigned to the D and G bands, respectively, which are typical bands of graphitic materials. The G band is a zone center vibration mode of graphite, whereas the D band is related to the defects and disordered carbonaceous solid [14,15]. The relative intensity ratio value (I_G/I_D) is applied to describe the defects of carbon materials. The I_G/I_D value of the CNT paper is ca. 3.1, which indicates that the CNT paper has a good structural integrity. The sharp and narrow bands further suggest the high graphitization degree of the CNT paper.

Fig. 2a shows the discharge/charge profiles of the Na–O₂ battery at a current density of 500 mA g⁻¹ (0.1 mA cm⁻²). The cathode is prepared by pressing a CNT paper onto a Ti mesh that functions as a current collector and without the use of any binder and conductive additives. The battery is cycled between 1.8 and 4.2 V (vs. Na⁺/Na, the same below) with 0.5 M NaSO₃CF₃ in diethylene glycol dimethyl ether (NaSO₃CF₃/DEGDME) as the electrolyte. The discharge plateau located at about 2.2 V is very flat. The discharge capacity reached 7530 mAh g⁻¹, which, to the best of our knowledge, is the highest value obtained at the same current density. The charge plateau is about 2.4 V, and the discharge/charge potential gap is only 200 mV. The charge capacity is about 3300 mAh g⁻¹, which results in an initial coulombic efficiency of 43.8%. The achieved reversible charge capacity is also higher than that reported previously at the same current density [9,16,17]. The discharge/charge capacity of the second cycle is about 3100 mAh g⁻¹ and 1300 mAh g⁻¹, respectively. The plateau voltages are similar to those in Hartmann's report, but the capacity is much higher than that reported at a low current density of 300 mA g⁻¹ [9]. In Liu's work, the reversible capacity is about 6000 mAh g⁻¹ at a current density of 300 mA g⁻¹, but the potential gap is very large, even larger than that of Li–O₂ batteries [16], and the capacity is only 1428 mAh g⁻¹ at 500 mA g⁻¹ [16]. In our current study, the discharge/charge potential gap is relatively small and the capacity is very high even at a current density of 500 mA g⁻¹. This result can be attributed to the 3-dimensional (3D) interpenetrating network of the CNT paper, which provides a large void space (see Fig. 1a) to accommodate the discharge product and to facilitate fast electron transport, especially during the charging process. With a limited

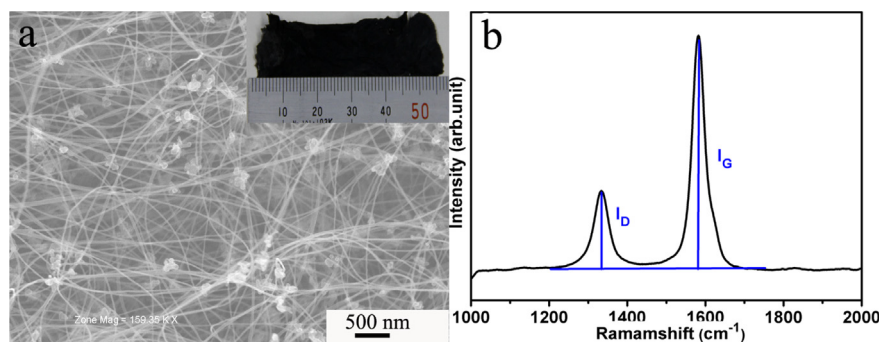


Fig. 1. SEM image (a) and Raman spectrum (b) of a CNT paper. The inset shows an optical image of the CNT paper.

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